THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

CONDUCTIMETRIC STUDIES OF THE KINETICS OF CRYSTALLISATION AND DISSOLUTION OF SPARINGLY SOLUBLE SALTS.

by

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PREFACE

The work described in this thesis was carried out in the period October 1955 to October 1958 at the University of Glasgow in the department of Physical Chemistry, which is under the supervision of Professor J. Monteath Robertson, F.R.S.

The work on the crystallisation of silver chromate and the dissociation constant of the hydrogen chromate ion has been published in two papers in the Transactions of the Faraday Society : reprints of both papers are appended to this thesis.

My thanks are due to the Department of Scientific and Industrial Research for a Maintainance Grant, during the tenure of which this work was performed.

I would also like to thank Mr. J. Leslie who constructed the conductivity cells and Mr. J. Findlay who has kindly provided the reproductions of the figures. Thanks are also due to Mr. A. Lawrie who gave technical assistance throughout the work.

Finally I wish to express sincere appreciation for the unfailing help and encouragement given me by Dr. G.H. Nancollas, under whose supervision this work was carried out.

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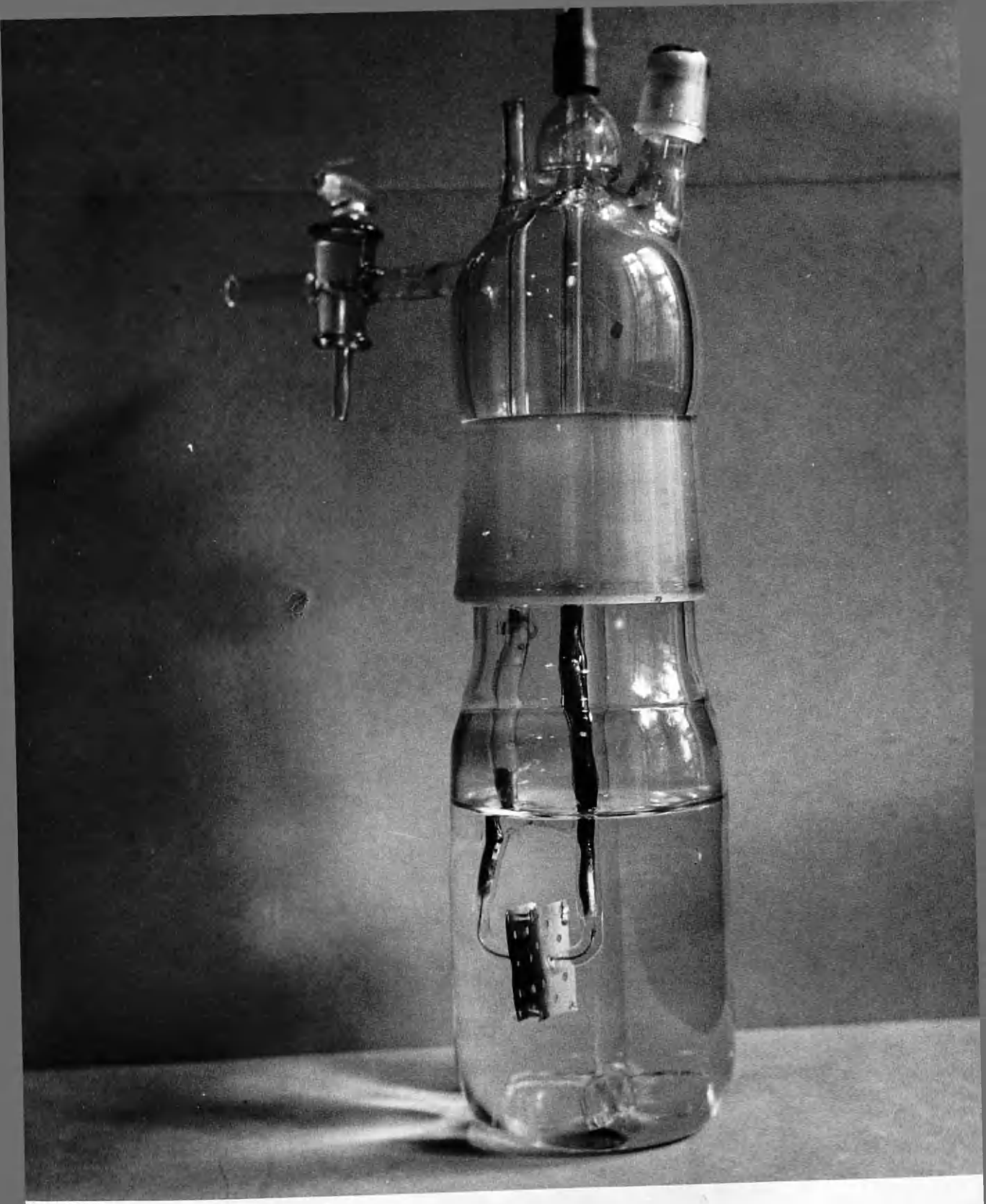


GENERAL INTRODUCTION

Heterogeneous reactions such as crystallisation and solution may be controlled by a purely physical process of transport of ions to the surface or by chemical reactions (including adsorption) which occur at the crystal surface. Sometimes a combination of both physical and chemical processes appears to control the rate of reaction.

In recent years a considerable volume of work has been published on the spontaneous crystallisation of various salts from aqueous solutions and it is considered that this is a two stage process: the formation of crystal nuclei, identified as an induction period, and their subsequent growth. A critical survey of most of the work particularly concerned with the kinetics of spontaneous precipitation has been made by Arne Nielsen[1] and he discusses the theories which have been put forward to interpret the kinetics.

The precipitation of barium sulphate was investigated by conductivity and light scattering methods by

Collins and Leineweber[2] who concluded that it involved nucleation, occurring as a single burst, followed by diffusion controlled growth of the nuclei in the super-saturated solution. Turnbull[3] also studied the barium sulphate system and found that nucleation was instantaneous but that precipitation was not diffusion controlled. Duke and Brown[4] considered that nucleation was a much slower process than growth and that stable nuclei contained several tens of molecules. Using a flow technique, Christiansen and Nielsen[5] measured the time of appearance of a definite fraction of precipitate when equivalent solutions of various concentrations of the two components were mixed. The systems studied were $BaCl_2 + H_2SO_4$ and $AgNO_3 + K_2CrO_4$. They found that the reaction velocity, S, of the overall precipitation, obeyed the equation :

$$S = k_p c^p ,$$

where c was the instantaneous concentration and k and p were constants. The value of p was 8 for barium sulphate and 6 for silver chromate and they suggested that nuclei or 'germs' capable of growth contained eight ions for the barium sulphate system and six for silver chromate, precipitation being a step-wise addition of ions. Aggregates of ions smaller than a germ were called clusters and a

germ was distinguished from a cluster by its much greater ability to capture and retain ions.

From studies of the production and growth rates of crystal nuclei of silver chromate and silver chloride Kobayashi[6,7] found the relationship

$$I\left(\frac{c - c_o}{c_o}\right)^n = K \quad , \quad \text{where} \quad c_o = \text{solubility},$$

between the induction period I and the supersaturation: $n = 3$ for silver chromate and $n = 2$ for silver chloride. The subsequent decrease in supersaturation attributed to growth, satisfied the equation

$$-\frac{dc}{dt} = K\,(c - c_o)$$

Johnson and O'Rourke[8], investigating the kinetics of precipitation of barium sulphate conductimetrically, obtained results which led them to believe that the precipitation was controlled by a reaction in the surface proportional to the area and to the fourth power of the concentration of reacting ions $(c - c_o)$. These authors interpreted a translation of the papers of Kobayashi[6,7] as implying second order kinetics for the growth of silver chloride. Although the Japanese is ambiguous in parts,

it would appear from Kobayashi's second paper[7] that the value $n = 2$ refers to the equation involving the induction period and not to the growth equation. Cobbett and French[9] have shown that in the equation

$$-\frac{dc}{dt} = K (c - c_o)^n$$

for the spontaneous precipitation of barium sulphate, n changes from 1 to 3 in the course of the precipitation.

The diversity in the conclusions of the above workers points to the multiplicity of factors to be considered in the spontaneous crystallisation process. If the growth step could be studied separately while controlling supersaturation and surface area, it would lead to simplification in the interpretation of results.

Ostwald first suggested that the supersaturation side of the solubility curve could be divided into two distinct regions: the 'metastable' and 'labile' regions. Inoculation was necessary to start the process of crystallisation in the metastable region and crystallisation would then take place only by deposition on the seeds, no new crystals being formed. At a well-defined supersolubility, the solution passed into the labile region,

where spontaneous crystallisation and nucleus formation would occur. Miers and his co-workers[11-14] supported this idea and showed that the variation of critical supersolubility with temperature could be represented by a supersolubility curve for many substances. This sharp demarcation between metastable and labile regions was criticised by de Coppet[15] and the conception was modified to imply that crystallisation was slow and difficult in the metastable region and fast and easy in the labile region, the transfer from one region to another being gradual. In support of Ostwald's original hypothesis, the more recent work of Davies and Jones[16] has shown that supersaturated solutions of silver chloride in which the ionic product was nearly 75% greater than the normal solubility product, could be kept stable for considerable periods of time. The critical supersaturation was determined within narrow limits.

Davies and Jones[17] prepared supersaturated solutions of silver chloride in a conductivity cell, inoculated them with seed suspensions and followed the resulting crystal growth by measuring the decrease in the conductivity of the solutions. Under these exactly reproducible conditions no new nuclei were formed and the net change in surface area due to growth was a small fraction of the total

initial surface of the seed crystals. The supersaturation could be derived at any stage in the crystallisation and it was found that the rate of crystal growth

$$-\frac{dc}{dt} = K (c - c_o)^2 ,$$

indicating a chemical reaction as the rate-determining step.

In the first part of the present work a study of the crystal growth of the 1:2 electrolyte, silver chromate, under similarly controlled conditions has been made. Accurate data for the solubility and critical concentration product have also been obtained.

In the spontaneous crystallisation experiments discussed previously, two groups of workers have suggested that the rate of crystal growth is diffusion controlled.[2,6] In the experiments of Collins and Leineweber sulphate ions for $BaSO_4$ precipitation were generated in situ by the interaction of persulphate and thiosulphate ions. The presence of these extraneous ions, however, seems to be an unnecessary complication. La Mer and Dinegar[18] and Bunn[19] considered that diffusion played some part in determining the rate of crystal growth. Most of the spontaneous

crystallisation results and the work of Davies and Jones, however, indicate that $n > 1$ in the crystal growth equation

$$-\frac{dc}{dt} = K (c - c_o)^n \quad .$$

At first sight it might be considered that crystallisation and solution are exactly reciprocal processes. Noyes and Whitney[20] studied the dissolution of rods of benzoic acid and lead chloride into water and expressed their results by the first order equation

$$\frac{dc}{dt} = K (c - c_o) \quad .$$

This points to a diffusion controlled process, and similar results were obtained by Bruner and St. Tolloczko[21] and Nernst[22]. The rate of solution of silver chloride seed crystals into water has been studied by Davies and Nancollas[23] who found that it followed the equation

$$\frac{dc}{dt} = K (c - c_o)^{3/2}.$$

While this cannot be interpreted as a simple diffusion-controlled process, it is certainly different from the case of crystal growth. From these results crystallisation

and solution reactions do not appear to be controlled by the same process.

In order to provide further data on the kinetics of solution of sparingly soluble salts, the second part of the present work, an investigation of the rate of solution of silver chloride and silver chromate, was undertaken.

Experiments to study the effect of impurities on the habit modification of various salts have been made[24-26] and are important in providing further information for the elucidation of crystallisation processes. Davies and Nancollas[27,28] have shown that surface active agents have a profound effect on the growth of silver chloride seed crystals. Part 3 of the present work continues the study of the influence of adsorbates. An attempt to study the effect of variation of ionic strength has also been made.

An account of a potentiometric study of the equilibrium

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{--}$$

is included as an appendix to the present work.

APPARATUS AND EXPERIMENTAL TECHNIQUES

The crystal growth of silver chromate was studied by measuring the change in conductivity which occurred when seed crystals were added to supersaturated solutions in conductivity cells. These solutions were prepared by adding solutions of silver nitrate and potassium chromate of known concentration to weighed quantities of conductivity water in the cells. Dissolution of silver chloride and of silver chromate was followed in exactly the same way, seed crystals being added to subsaturated solutions of the corresponding electrolyte.

Measurement of Resistance.

Resistances were measured on an a.c. screened Wheatstone bridge of the type described by Jones and Joseph[29] and by Shedlovsky[30] and incorporating the recommended modifications for minimising effects due to the inductance and capacity of various parts of the bridge network.

The circuit was as shown in figure 1. R_1 was the cell and R_2 was a Sullivan non-reactive resistance box, reading from 10,000 to 0.1 ohm. The ratio arms R_3 and R_4 were supplied by a 100 ohm Sullivan non-reactive slide resistance, and the total resistance was subdivided into 10^5 parts by two concentric dials. The output from the bridge was amplified before passing to the ear-phones by a two stage high gain mains operated Sullivan amplifier. The oscillator, a mains operated Advance model, giving frequencies from 15 to 15,000 cycles per second, was placed about six feet from the bridge to prevent interaction and measurements were normally taken at an optimum frequency of 1,000 cycles per second. Screened and grounded leads connected the oscillator to the bridge via a Sullivan balanced and screened transformer, designed to screen effectively the supply source from the bridge without upsetting the balance of the latter to earth. The sharpness of the sound minimum in the detector was improved considerably by earthing the bridge. A modified Wagner earth described by Jones and Joseph[30] ensured the telephone earpiece being maintained at ground potential, thus eliminating any leakage of current due to capacity between the telephone coils and the operator. In the figure it is

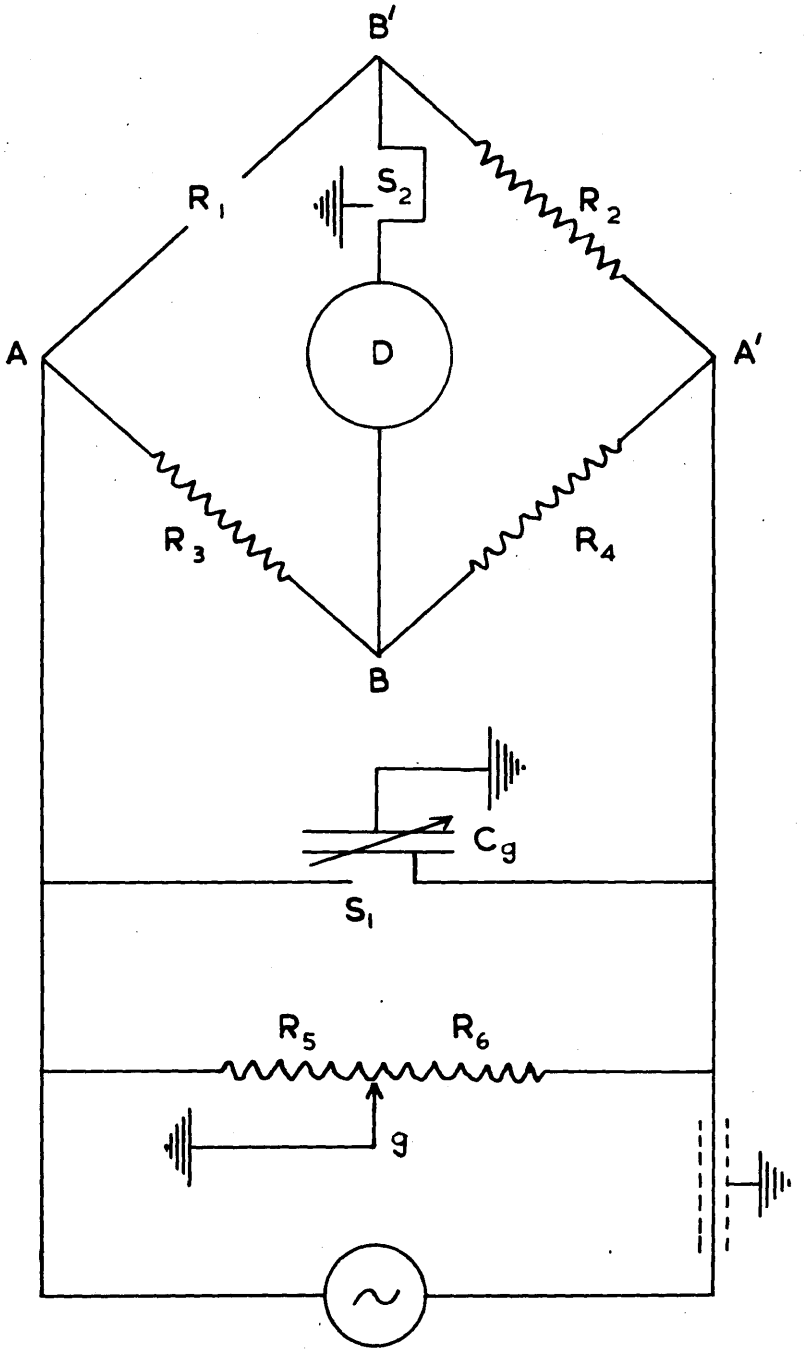


FIGURE 1

represented by the resistances R_5, R_6, the contact g, and the variable condenser C_g. The bridge was balanced in the usual way and the detector D was connected to ground by switch S_2. B was then brought to ground potential by adjustment of the contact g. The bridge was again balanced and the process repeated if there was any change.

Connections to the cell were made by taking leads from the electrodes to two mercury cups supported in the thermostat. This prevented heat interchange to the room from the cell. Any resistance effect due to the leads from the mercury cups to the bridge was compensated by having an equal length of identical wire connecting the resistance box R_2 to the circuit. A Sullivan decade stable mica condenser, reading from 0 to 0.01 μF, could be connected across R_2 or the cell in order to compensate for capacity effects. The connections to the cell and the resistance box could be interchanged by means of a commutator of the rocking type.

In practice when measurements were taken, the Wagner earth was balanced as described above and the capacity and resistance R_2 were adjusted until no sound was detected in the earphones. It was found that the setting of the Wagner earth could be kept constant: any

slight deviation being easily compensated by the mica condenser.

When water and solutions of high resistance were being measured a 10,000 ohm, non-reactive, standard resistance was connected in parallel with the cell.

Temperature Control.

The cell was supported in a large, earthed, metal thermostat which was heat insulated and contained Shell Diala Oil B to prevent capacity errors[30]. The oil was stirred efficiently by an electrically driven paddle system. The thermostat contained a tray carrying two small water thermostats with covers in which bottles of seed suspension were stored in darkness. A toluene-mercury spiral regulator operating a 60 watt red lamp through a vacuum relay, maintained the temperature of the oil at $25^{\circ} \pm 0.005^{\circ}C$. A booster heater was also provided. The Beckmann thermometer used was checked periodically with a platinum resistance thermometer which had been constructed and calibrated at the triple point of water and at various other temperatures by V.S.K. Nair[31], using an N.P.L. platinum resistance thermometer. To prevent excessive condensation of moisture in the cap of the cell, an

Anglepoise lamp with a red bulb was fixed at a convenient distance to keep the cell cap at a temperature about one degree lower than that of the bath. The thermostat temperature was maintained between experiments so that seed crystals would age at the same temperature as that at which they would subsequently be used.

Conductivity Cell.

The heterogeneous nature of crystallisation and solution requires efficient stirring of the cell to make a quantitative study of the processes possible.

The cell used was of the Hartley-Barrett[32] type, made throughout of Pyrex glass and with dipping electrodes of greyed platinum (Plate 1). It is difficult to seal platinum to Pyrex glass: to overcome this difficulty about one-eighth of an inch of Araldite epoxy resin powder was introduced into the bottom of the electrode supports, and the cell was placed in an oven at 60°C to cure the Araldite, forming a permanent seal which prevented any leakage of mercury into the cell solution. The electrodes were situated near the walls of the cell so that an efficient four-bladed glass stirrer could be supported from a pulley shaft through a central aperture in the cell cap. The

stirrer was driven by a small electric motor: the speed of stirring could be varied by means of a rheostat. The stirrers in the cell and thermostat were turned off for a few seconds when taking bridge readings. A small glass hood, attached to the stem of the cell stirrer, prevented contamination of the cell contents by foreign matter falling through the aperture in the cap. A side tube in the cap with a three-way tap enabled carbon dioxide-free air to be passed over the solution in the cell. Additions of solution and seed were made by pipette through a short tube in the cell cap which was fitted with a ground glass cap.

The purified carbon dioxide-free air was obtained by filtering compressed air through a large jar packed with cotton wool. The air stream then bubbled through 2N sulphuric acid and 30% potassium hydroxide in two tubes and a tower packed with glass beads and short lengths of glass tubing. This was followed by two water scrubbers and a column of distilled water. Finally, the air stream passed through conductivity water, a preheating tube and cotton wool pad supported in the thermostat, so that it was saturated with water vapour at 25°C before entering the cell.

Preparation of Conductivity Water.

For all the conductivity experiments, the water was prepared by a mixed bed deionization process[33]. Distilled water was passed down a Pyrex glass tube, with a sintered disc at the bottom, filled with an intimate mixture of a strong acid and a strong base resin. Any cation impurities were replaced by hydrogen ions from the strong acid resin and these were immediately neutralised by hydroxyl ions from the basic resin. Anions were removed by the strong base resin in the same way. The specific conductivity of the product at 25°C remained steady at about 0.1×10^{-6} $ohms^{-1}$.

For the silver chromate crystallisation experiments, the resins used were Nalcite SAR and Nalcite HCR. After at least 600 litres of distilled water had been treated, these resins were replaced by the strong acid resin Amberlite IR 120 and the strong base resin Amberlite IRA 400. Before the latter resins were used they were regenerated as follows:

> 50 mls. of Amberlite IR 120 in a chromatographic column were treated with a litre of 1N hydrochloric acid and then washed with distilled water to a pH~7 (Universal indicator).

After conversion to chloride form 100 mls. of Amberlite IRA 400 were treated with carbonate-free sodium hydroxide and washed till pH 7-8. This procedure converts bivalent ions such as carbonate to univalent chloride, which are then more easily replaced by hydroxyl ions.

Two parts of the strong base resin IRA 400 and one part of the strong acid resin IR 120 were then simultaneously added to the deionisation column. This ensured an intimate mixture despite the difference in density of the resins. The column was washed with several litres of distilled water and the specific conductivity of the water then produced was 0.12×10^{-6} $ohms^{-1}$.

Conductivity water for the preparation of solutions was collected in a Pyrex receiver fitted with a soda-lime guard tower.

Preparation of Stock Solutions.

Steamed out, seasoned Pyrex flasks were used for the preparation of stock solutions, which were usually about 0.1N for silver chromate and 0.01N for silver chloride.

A.R. potassium chloride was recrystallised four times from conductivity water. The crystals were then

placed in a platinum dish and dried in an electric oven at 120°C. Samples were heated to dull red heat in a platinum dish and allowed to cool in a desiccator before use. A.R. potassium chromate was recrystallised twice from conductivity water and the crystals were thoroughly dried before storing. A.R. silver nitrate was used without further purification. All reagent bottles were protected with dust caps. Samples of the reagents were weighed out from small Pyrex weighing bottles using a Stanton Model S.M.1 balance and platinum plated weights which had been calibrated by the method of Kohlrausch[34]. Solutions were made up by weight from conductivity water using a Sartorius balance of capacity ~ 2 Kg. and weights which had also been calibrated. This balance was sensitive to 0.005g. and all weighings were corrected to vacuum weight.

Dilute solutions of silver nitrate and potassium chromate used in the crystallisation experiments were accurately made up by weight from these more concentrated stock solutions. Fresh dilute solutions were prepared for each experiment so that they should be free from any foreign matter which might endanger the stability of the supersaturated solutions in the cell. In some experiments, dilute solutions of potassium chromate were made

by exactly neutralising stock solutions of chromic acid with standard carbonate-free potassium hydroxide[35]. The stock solutions of chromic acid were prepared from A.R. chromic oxide which had been thoroughly dried in an oven at 120°C, cooled in a desiccator and weighed out of contact with air owing to its hygroscopic nature. This second method of preparing potassium chromate was used in investigating the influence of hydrolysis on the crystallisation of silver chromate.

Determination of Cell Constant.

The cell constant was determined by the method of Frazer and Hartley[36]. The cell was first dried, weighed, rinsed with conductivity water several times, and swept free of carbon dioxide by passing a stream of purified air through it for about half an hour. The purified air stream previously described could be diverted to pass into the cell as it was filled directly from the resin column. Conductivity water was added dropwise into the cell until the level was half an inch above the top of the electrodes. The cell was reweighed, placed in the thermostat and connected into the circuit. Throughout the determination the stirrer revolved at a constant rate of about 500 revs.

per minute and a fairly rapid stream of purified air was passed through the cell. The conductivity of the water was measured at half-hourly intervals until a constant bridge reading was obtained. This usually required about three to four hours and, under test, it was shown that this steady value could be maintained for at least eight hours. About 2g. of an approximately 0.01 N potassium chloride stock solution was then added to the water in the cell from a weight burette, and the stirring was resumed until the resistance became constant. The setting of the resistance box was adjusted until the bridge readings for the two positions of the commutator were close together. The bridge readings were determined for two settings of the resistance box. The cell was stirred between all readings and the readings were taken as rapidly as possible to avoid heating effects in the cell. Four or five further additions of stock solution were made, repeating the same series of operations after each addition, until a concentration of about 0.001 N was obtained in the cell. The cell was then removed from the thermostat, its outer surface was cleaned and dried and the whole reweighed: the weight of water in the cell was evaluated from the known weights of potassium chloride solution added. This was always within 0.1 g. of the original weight of water

introduced, indicating that the amount of evaporation during an experiment was negligible.

The cell constant was then calculated by comparing each measured value with the conductivity values derived by Shedlovsky[37] at the same concentrations, using the interpolation formula[38]

$$\Lambda = 149.92 - 93.85\ c^{\frac{1}{2}} + 50\ c.$$

The value of the cell constant for each cell used in the crystallisation work was evaluated from at least twelve determinations (three series). Cell A, working capacity about 450 g., had a cell constant of 0.03696 ± 0.03%. Cell B had a capacity about 250 g. and was broken once in the course of the work. Its cell constant of 0.06191 ± 0.03% became 0.06897 ± 0.03% after repair. The cell constant of cell E, capacity 250 g., was 0.07800 ± 0.03%.

The cell constants of the unstirred Hartley-Barrett type cells, used in determining the critical concentration product of silver chromate, were obtained by using the conductivity values for 0.01 demal potassium chloride solutions given by Jones and Bradshaw[39]. Each cell was cleaned, filled with conductivity water and placed in the thermostat. Resistance readings were taken after half an hour when

temperature equilibrium was obtained. The cell was emptied, rinsed several times with an exactly 0.01 demal solution of potassium chloride, filled with the same solution, and again allowed to equilibrate in the thermostat. The resistance was measured and compared as before with the known conductivity of 0.01 M potassium chloride solution at 25^{0}C: 0.0014087 $ohm.^{-1}cm.^{-1}$. The values obtained for the cell constants were 0.1286 for cell C and 0.1067 for cell D.

Measurement of pH.

The influence of pH in determining the ion species present in chromate solutions is well established and has been studied by several workers[35, 40-42]. Its significance in solubility and silver chromate kinetic experiments will be discussed later.

pH measurements were made with a Doran pH meter using a Cambridge glass and calomel electrode assembly. The apparatus was standardised with the buffer solutions 0.05 M potassium hydrogen phthalate, pH = 4.005[43], and B.D.H. tabloid phosphate buffer, pH = 6.99.

The solutions for pH determination were contained in a three-necked Quickfit round-bottomed 250 ml. flask. Near the top there was a small tube fitted with a ground

glass stopper which was used for making additions to the cell and also acted as an inlet for nitrogen, which was passed over the cell solution throughout the experiment. The vertical side neck of the flask supported the glass electrode in a rubber collar. The calomel electrode was held similarly in the other side neck. A Pyrex glass link stirrer supported in a Quickfit stirrer gland occupied the centre neck of the flask and was driven by a stirrer motor. The positions of the electrodes in the cell were adjusted so that the solution in the flask could be efficiently stirred at approximately 500 revs./min.

The cell was clamped in a glass thermostat filled with water and maintained at $25^{\circ} \pm 0.01^{\circ}C$ by means of a heating bulb operated by a toluene-mercury regulator through a Sunvic vacuum relay type F 102/4. The thermometer used in the thermostat was standardised as previously described.

Spectrophotometric Measurements.

Spectrophotometric measurements were used as an independent check on the solubility of silver chromate.

The saturated solutions were prepared in a Pyrex glass saturator (figure 2), similar in type to that described by Davies[44], fitted with a No.3 sintered glass disc.

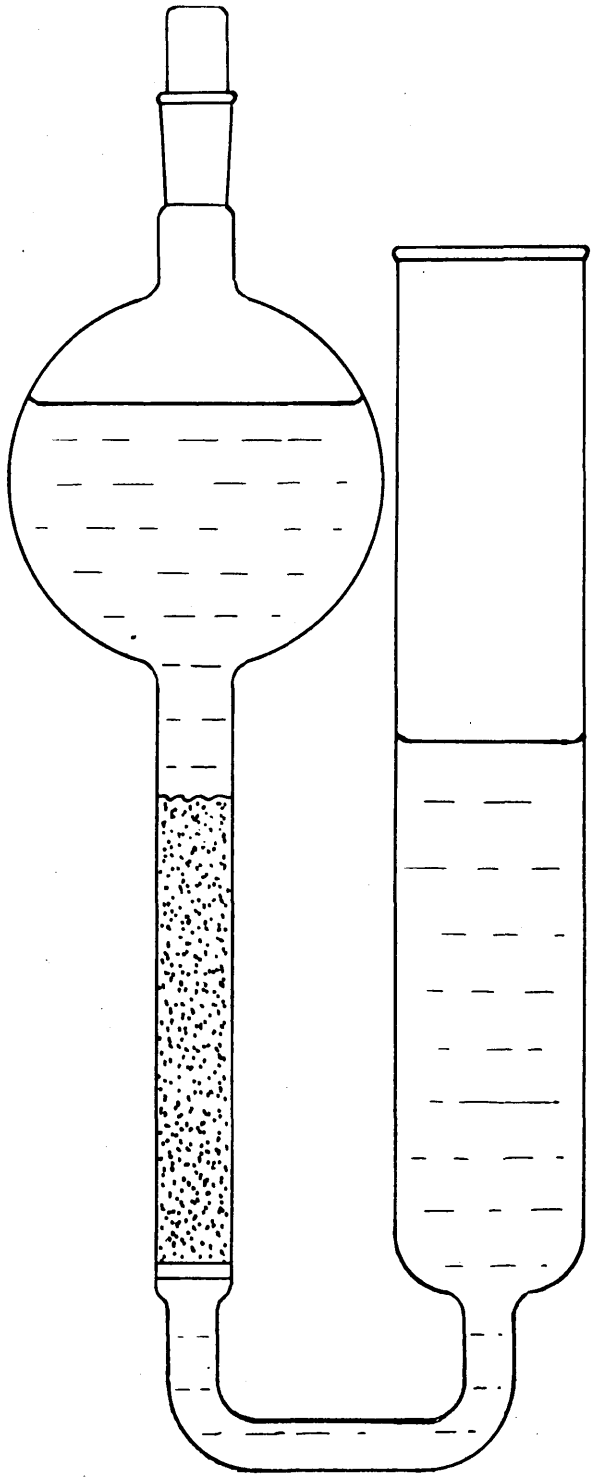


FIGURE 2

For one experiment recrystallised silver chromate was stirred with conductivity water in a Quickfit flask and samples of saturated solution were withdrawn by means of a pipette with a No.2 sinter filter stick attached at the end. The saturator and the flask were supported in the thermostat at 25°C.

Optical densities were obtained with a Unicam spectrophotometer model S.P. 500, using 1 cm. quartz cells for all experiments.

Grade A glassware was used in all experimental work.

PART 1

CRYSTALLISATION OF SILVER CHROMATE

INTRODUCTION.

Assuming that crystal growth of a sparingly soluble salt involves three steps: diffusion of solute to the surface, deposition of ions on the crystal face and the opposing process of solution, Davies and Jones[17] have interpreted the second order kinetics for the growth of silver chloride seed crystals in terms of stationary concentrations of silver and chloride in an adsorbed layer of hydrated ions at the crystal surface. Davies and Nancollas[23] have found that the temperature coefficient of crystallisation of silver chloride is unity and from experiments at non-equivalent initial ionic concentrations of silver and chloride, have provided further evidence for the above picture of crystal growth. In the presence of surface-active agents[27] the rate of crystallisation is reduced, and when supersaturated solutions were inoculated with seed crystals previously aged in these adsorbates[28], the crystals did not grow immediately. This behaviour was explained in terms of adsorption by assuming that the surface of the seed crystals had to be freed from adsorbed impurity in the supersaturated solution before growth was

possible. As would be expected in a reaction dependent on available surface area, the length of the induction period was inversely proportional to the quantity of seed added.

Van Hook[45] observed similar induction periods in the growth of silver chromate seed crystals aged in aqueous solutions which he attributed to nucleation: progressive addition of seeds continuously diminished the length of the induction period and increased the rate of the main part of the crystallisation curve. In his experiments the constant value used for the initial ionic product $[Ag^+]^2[CrO_4^=]$ of the supersaturated solution was 50×10^{-12} moles/l. This value is well in excess of the critical concentration product – the ionic product at which spontaneous crystallisation becomes possible – determined in the present work.

It was considered likely that the induction periods in the crystal growth of silver chromate observed by van Hook were caused by adsorbed impurities on the surface of his seed crystals. If this were so and unpoisoned seed crystals could be prepared, it would be of interest to see if Davies' picture of crystallisation can be applied not only to a 1:1 electrolyte but also to one of higher valence type, silver chromate. This work is described in the results section of Part 1.

RESULTS

1. Determination of Solubility.

The solubility data available in the literature for silver chromate showed values varying from 0.603×10^{-4} moles per litre to 0.907×10^{-4} moles per litre.[46,47] An accurate solubility value is an essential prerequisite for kinetic studies and it has been determined by two different methods in the present work.

Conductimetric experiments.

Saturated silver chromate solutions were obtained in a conductivity cell by approaching equilibrium from both the subsaturated and supersaturated regions.

In the subsaturation experiments the conductivity cell was rinsed six times with conductivity water, connected to the carbon dioxide - free air supply and filled directly from the resin column. The cell was then placed in the thermostat, connected to the circuit and the contents stirred in a stream of carbon dioxide - free air. The steady resistance of the water was recorded after about two

hours. A measured volume of seed suspension was then added to the water and resistance readings were noted at various times until the final steady resistance was taken after several days. Slight impurities in the seed suspension were corrected for by adding a further small volume of seed suspension and noting any change in resistance. The specific conductivities of the water and of the impurities in the seed suspension were subtracted from the observed conductivity to give the specific conductivity of the saturated silver chromate solution.

The saturated concentration of silver chromate was approached from the supersaturated region by allowing a crystallisation experiment (page 42) to come to equilibrium: the final steady resistance was then noted and correction made for impurities in the seed suspension. In this experiment the saturated solution contains K^+ and NO_3^- ions from the known concentrations of potassium chromate and silver nitrate added to the cell. The specific conductivities of these ions, determined by using the mobility values $\Lambda^o_{K^+} = 73.52$ [48] and $\Lambda^o_{NO_3^-} = 71.44$ [48] in the appropriate Onsager equations,[49]

$$\kappa_{K^+} = 73.52 - 46.67\sqrt{c} \text{ , and}$$

$$\kappa_{NO_3^-} = 71.44 - 46.19\sqrt{c} \text{ ,}$$

were subtracted from the observed conductivity and the specific conductivity of saturated silver chromate was then evaluated as described above.

In the conductimetric determinations of the solubility in which experiments must be carried out over a period of days, a slight fluctuation was detected in the equilibrium value of the conductivity. The pressure of the compressed air supply is subject to some variation when used continuously for long periods and this and slight evaporation will disturb the equilibrium

$$H^+ + CrO_4^= \rightleftharpoons HCrO_4^-$$

existing in the saturated silver chromate solution in the cell and some variation in the accurately measured equilibrium conductivity value can be expected. Careful control of conditions, however, usually gave reliable readings.

The pH of saturated silver chromate solutions was measured under exactly the same conditions as in the conductivity experiments and found to be 7.3,

$$\text{i.e.} \qquad pH = -\log\{H^+\} = -\log[H^+]f_{H^+} = 7.3 \quad ...(1)$$

Potentiometric measurements which will be described in the appendix to the present work yielded a value for the

dissociation constant, k_a , of the hydrogen chromate ion ($HCrO_4^- \rightleftarrows H^+ + CrO_4^=$) at 25°C of

$$k_a = \{H^+\}\{CrO_4^=\}/\{HCrO_4^-\} = 3.03 \times 10^{-7} \text{ moles/l.} \quad ...(2)$$

Davies and Prue[42] have measured the equilibrium constant for the reaction $Cr_2O_7^= + H_2O \rightleftarrows 2HCrO_4^-$ and given the value at 25°C as

$$k_b = \{HCrO_4^-\}^2/\{Cr_2O_7^=\} = 3.03 \times 10^{-2} \text{ moles/l.} \quad ....(3)$$

It follows that at pH 7.3 the concentration of dichromate ions in saturated silver chromate solutions is negligible and the total chromium concentration,

$$T_{Cr} = [CrO_4^=] + [HCrO_4^-] \quad .....(4)$$

The ionic strength, I , of a saturated silver chromate solution is given by the equation

$$I = 0.5\left([Ag^+]+[H^+]+4[CrO_4^=]+[HCrO_4^-]+[OH^-]\right) \quad .....(5)$$

From electroneutrality considerations,

$$[Ag^+] + [H^+] = [HCrO_4^-] + 2[CrO_4^=] + [OH^-] \quad .....(6)$$

Substituting (6) in (5),

$$I = T_{Cr} + 2[CrO_4^=] + [OH^-] \quad .....(7)$$

As a first approximation it was assumed that

$$T_{Cr} = [CrO_4^{=}] + 1 \times 10^{-4}$$

and $[OH^-]$ was negligible, and the activity coefficient, f, for each ion was obtained from the Davies equation[50]

$$-\log f = 0.51\, z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2\, I \right) \ldots\ldots\ldots (8)$$

where z_i is the valency of the ion, using the I value from equation (7). $[H^+]$ and $[OH^-]$ and $[CrO_4^{=}]/[HCrO_4^-] = \alpha$ were obtained from equations (1) and (2). The specific conductivity (κ) of saturated silver chromate solution, evaluated in the conductivity experiments, may be written

$$\kappa = \kappa_{Ag^+} + \kappa_{CrO_4^{=}} + \kappa_{HCrO_4^-} + \kappa_{OH^-} \quad \ldots\ldots (9)$$

assuming the electrolyte to be completely dissociated at these low concentrations.

Substituting the value of $[Ag^+]$ obtained from equation (6) in equation (9),

$$1000\,\kappa = 2[CrO_4^{=}]\Lambda_{\frac{1}{2}Ag_2CrO_4} + [HCrO_4^-]\Lambda_{AgHCrO_4} + [OH^-]\Lambda_{AgOH} + [H^+]\Lambda_{Ag} \quad \ldots\ldots (10)$$

The conductivities of silver chromate, silver hydrogen chromate and silver hydroxide were calculated from the Onsager equations[49]

$$\Lambda_{\frac{1}{2}\,Ag_2CrO_4} = 144.5 - 263.4\,[Ag_2CrO_4]^{\frac{1}{2}}$$
$$\Lambda_{AgHCrO_4} = 112.0 - 85.4\,[AgHCrO_4]^{\frac{1}{2}}$$
$$\Lambda_{AgOH} = 260.0 - 119.0\,[AgOH]^{\frac{1}{2}}$$

where $\Lambda^{o}_{Ag} = 61.92$ [48] and $\Lambda^{o}_{OH} = 197.6$ [51]. $\Lambda^{o}_{\frac{1}{2}\,CrO_4^{=}} = 82.5$ was obtained by extrapolation of available chromate conductivity data[52] and $\Lambda^{o}_{HCrO_4^{-}} = 50$ was estimated since the contribution made by this ion was a small fraction of the total conductivity.

From equation (10), using the value of α obtained from equations (1) and (2), the values of $[HCrO_4^{-}]$, $[CrO_4^{=}]$ and $[Ag^{+}]$ were calculated and the solubility of silver chromate

$$S = \sqrt[3]{([Ag^{+}]^2[CrO_4^{=}]/\,4)}$$

was obtained by successive approximations. The value of S from subsaturation experiments was 0.915×10^{-4} and 0.940×10^{-4}. The supersaturation experiment gave a value of 0.970×10^{-4}. The agreement is good in view of the appreciable corrections for hydrolysis which have to be made.

Spectrophotometric measurements.

The effects of hydrolysis on measurements of the conductivity of saturated silver chromate solutions have been discussed. Spectrophotometric measurements of the solubility allowed the system to be studied under conditions in which hydrolysis of the $CrO_4^{=}$ ion is suppressed.

Silver chromate, slowly precipitated from equivalent solutions of potassium chromate and silver nitrate (page 48), was washed thoroughly with distilled water and then with conductivity water by decantation. A 10 cms. column of the precipitate was introduced into the saturator shown in figure 2 and again washed by circulating several samples of conductivity water through the saturator. A final 40 ml. volume of conductivity water was allowed to circulate twice through the column: each circulation took about two hours. 10 ml. portions of the saturated silver chromate solution obtained were made up to 25 mls. with 0.05 N carbonate - free potassium hydroxide solution. This solution was centrifuged to remove precipitated silver hydroxide and the absorption of the clear solution was measured at 373 mμ, a maximum in the chromate ion spectrum. A sample withdrawn after a further circulation through the saturator showed the same optical density within experimental error.

Two experiments were carried out as described above. In a third experiment measurement was made of the optical density of a saturated solution obtained by stirring recrystallised silver chromate crystals (page 43) with conductivity water (page 25) and treating the solution in the same way. The mean optical density of the samples in these three experiments measured in a 1 cm. cell was 0.2356.

The extinction coefficient of a standard 0.00103 M potassium chromate solution made 0.05 N with respect to potassium hydroxide was measured at 373 mμ and found to be 4800. An identical value had been obtained by Vandenbelt[53].

The chromate ion concentration calculated from the mean optical density of the saturated silver chromate solutions was 1.227×10^{-4} moles/l. The pH of these solutions in equilibrium with air was found to be 6.7, so that $HCrO_4^-$ ions and traces of $Cr_2O_7^=$ ions would be present in the solution and, when it was made alkaline, they would be converted to $CrO_4^=$ ions. The above chromate ion concentration therefore represented the total chromium content of the solution, T_{Cr}, and

$$T_{Cr} = [CrO_4^=] + [HCrO_4^-] + 2[Cr_2O_7^=] = 1.227 \times 10^{-4} \text{ moles/l.} \quad \text{.....(11)}$$

From equations (2), (3) and (11),

$$T_{Cr} = [HCrO_4^-]\left(1 + \frac{k_a f_1}{\{H^+\}.f_2}\right) + [HCrO_4^-]^2\left(\frac{2f_1^2}{k_b.f_2}\right) \quad ...(12)$$

where f_1 and f_2 are the activity coefficients for uni- and divalent ions respectively. From electroneutrality considerations,

$$[Ag^+]+[H^+] = 2[CrO_4^=] + [HCrO_4^-] + 2[Cr_2O_7^=] + [OH^-] \quad ...(13)$$

Substituting (11) in (13),

$$[Ag^+] + [H^+] = T_{Cr} + [CrO_4^=] + [OH^-] \quad .....(14)$$

From equations (11) and (14), the ionic strength I could be expressed as

$$I = T_{Cr} + 2[CrO_4^=] + [Cr_2O_7^=] + [OH^-] \quad .....(15)$$

A first value of I was obtained by assuming that $[CrO_4^=] = 0.9 \times 10^{-4}$ and neglecting $[Cr_2O_7^=]$ and $[OH^-]$. The $[HCrO_4^-]$ was then evaluated from equation (12) and used in equation (3) to give the $[Cr_2O_7^=]$. The $[CrO_4^=]$ and $[Ag^+]$ were then obtained from equations (11) and (13) and the solubility of silver chromate, $S = \sqrt[3]{([Ag^+]^2[CrO_4^=]/4)}$ was found to be 0.880×10^{-4} moles/l. This value is in

reasonable agreement with the conductimetric value, 0.915×10^{-4} moles/l., determined in the present work and with the solubility recently obtained by Sirůček [47] (0.907×10^{-4} moles/l.). It was used in the subsequent work; and the solubility product extrapolated to zero ionic strength is 2.44×10^{-12} moles^3 litres^{-3}.

2. Critical Concentration Product

It was necessary to find the value of the critical ionic product of silver chromate, $[Ag^+]^2[CrO_4^=]$, which was the limit of stability in supersaturated solutions.

Stock solutions of silver nitrate and potassium chromate were made up from conductivity water, and from these, fresh dilute solutions were prepared for each experiment. The concentrations of the dilute solutions were varied so that the concentration of silver chromate prepared in the cell during the run was some multiple of the solubility product (e.g. 3,6,8,24).

The conductivity cell C or D was rinsed with conductivity water and drained. 150 mls. of a dilute silver nitrate solution were then added to it, the cap was fitted and the cell was placed in the oil thermostat, connected

to the bridge, and the resistance of the silver nitrate solution was followed. When the reading was steady, 150 mls. of a dilute potassium chromate solution, previously equilibrated at 25°C, were added and the rise in resistance was followed first at 3 or 5 minute intervals and then at progressively longer time intervals, for periods ranging from 18 to 71 hours. The use of relatively large volumes of silver nitrate and potassium chromate solutions avoided local concentration effects which might cause crystallisation.

The experiments are summarised in Table 1 and the change in specific conductivity per hour over the first 18 hours of each experiment is plotted against the initial concentration product in figure 3. The approximately linear relationship, when extrapolated to zero change in conductivity, gives a value of approximately 10×10^{-12} $moles^3.litres^{-3}$ for the critical concentration product.

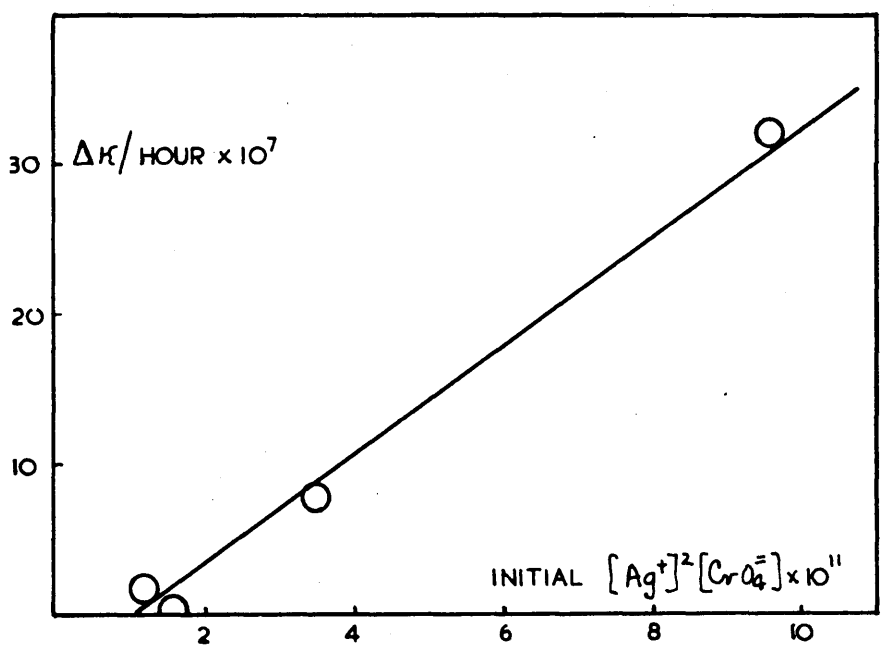
3. Seed Preparation and Crystal Growth

Crystallisation experiments could now be designed so that the concentration of the supersaturated solutions of silver chromate, prepared in the conductivity cell, was

TABLE 1

Run	Cell	Initial concentrations $[Ag^+]\times10^4$ moles/l.	$[CrO_4^=]\times10^4$ moles/l.	$[Ag^+]^2[CrO_4^=]$ x 10^{11}	Duration of experiment (hours)	$\Delta\kappa$/hr. x 10^7
5	C	2.88	1.44	1.20	18.5	1.75
6	D	3.91	2.00	3.51	70	7.7
7	C	5.77	2.88	9.61	71	32
9	D	3.17	1.59	1.60	21	0.2

FIGURE 3



greater than the solubility but less than the critical concentration.

The cell was filled with conductivity water in the manner described previously and was allowed to reach temperature equilibrium in the oil thermostat in a rapid stream of carbon dioxide - free air. When the resistance of the water had reached a steady value, 10 mls. of a dilute solution of silver nitrate were added to the cell from a calibrated pipette and the steady value of the resistance was recorded. This was followed by 10 mls. of a dilute potassium chromate solution added drop by drop over a period of approximately 6 minutes. The solutions were mixed very slowly in this way with stirring to avoid local concentration effects which would favour formation of crystal nuclei : the usual rate of stirring was approximately 500 revs./min.. The concentrations of the added solutions were such that the final concentration of silver and chromate ions in the cell were equivalent, and the ionic product was approximately twice the solubility product of silver chromate.

The stable supersaturated solution required about two hours to come to carbon dioxide and temperature equilibrium. There was a slight upward drift in the resistance readings after potassium chromate was added to the

cell. This was probably caused by hydrolysis but the change in resistance over one hour was less than 1 % of the change recorded during the first hour of crystallisation. This drift was minimised by adding a slight excess of potassium hydroxide to the potassium chromate solutions, prepared from chromium trioxide and potassium hydroxide.

After coming to temperature equilibrium, the required suspension of silver chromate seed crystals was quickly removed from the thermostat, shaken vigorously, and a homogeneous sample was withdrawn into a small clean and dry pipette. This was immediately added to the stirred solution in the cell, a stop-clock was started and the resistance reading was taken after the first half-minute. Bridge readings were recorded at one minute intervals and then at longer time intervals, for at least 30 minutes. In order that additions of seed suspension should be as quick as possible, pipettes with very short delivery times were used.

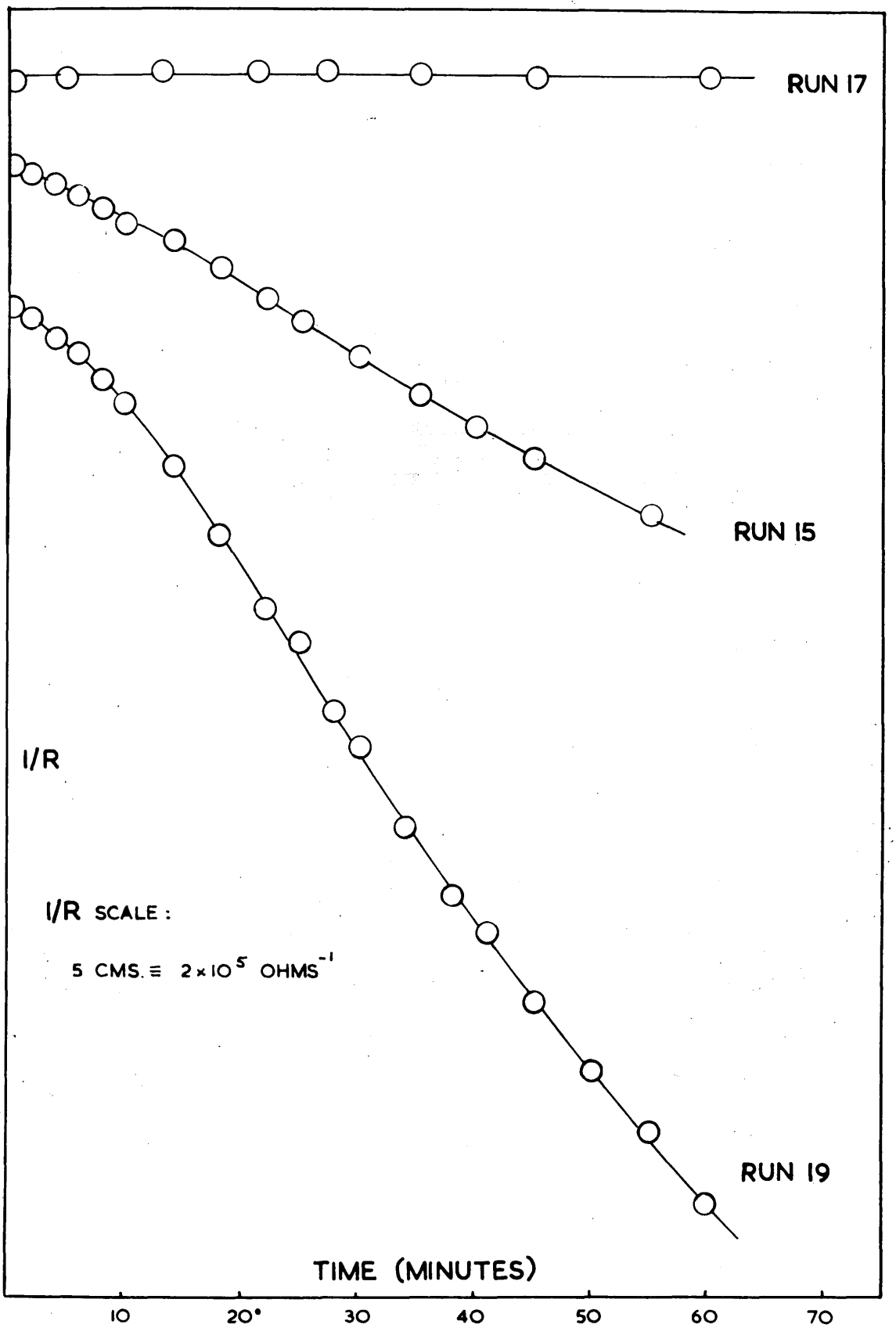
Seeds prepared by recrystallisation from aqueous solution.

Seed crystals consisting of needles of average length 40 μ, were prepared by crystallising silver chromate from boiling saturated solutions. This method, the one most likely to yield uniformity of size, has been used by Jones[16] and is described in detail for preparation of silver

chloride seed crystals (page 86). Silver chromate crystals prepared in this way and aged at 25°C would not allow crystallisation for at least two hours (Run 17). Washing the crystals before use reduced the induction period to 5 to 10 minutes, depending on whether the crystals were boiled in conductivity water (Run 15) or merely washed several times in hot conductivity water (Run 19) before being made up as the aqueous suspension for addition to the cell. The resistance of the solutions rose regularly at the end of the induction period. These results are represented in figure 4. It was not possible to remove the induction periods entirely by washing.

It was probable from the above results and those of van Hook[45] that the impurities adsorbed by silver chromate seed crystals were hydrolysis products. In an attempt to minimise hydrolysis silver chromate was recrystallised from dilute potassium hydroxide solution of pH ~ 11.5 and stored in the same solution. When these seeds were washed several times with conductivity water to remove the potassium hydroxide, and used for inoculation, the rate of crystallisation was slow but there was no trace of induction period. Work at higher pH values is impossible because of the formation of silver hydroxide.

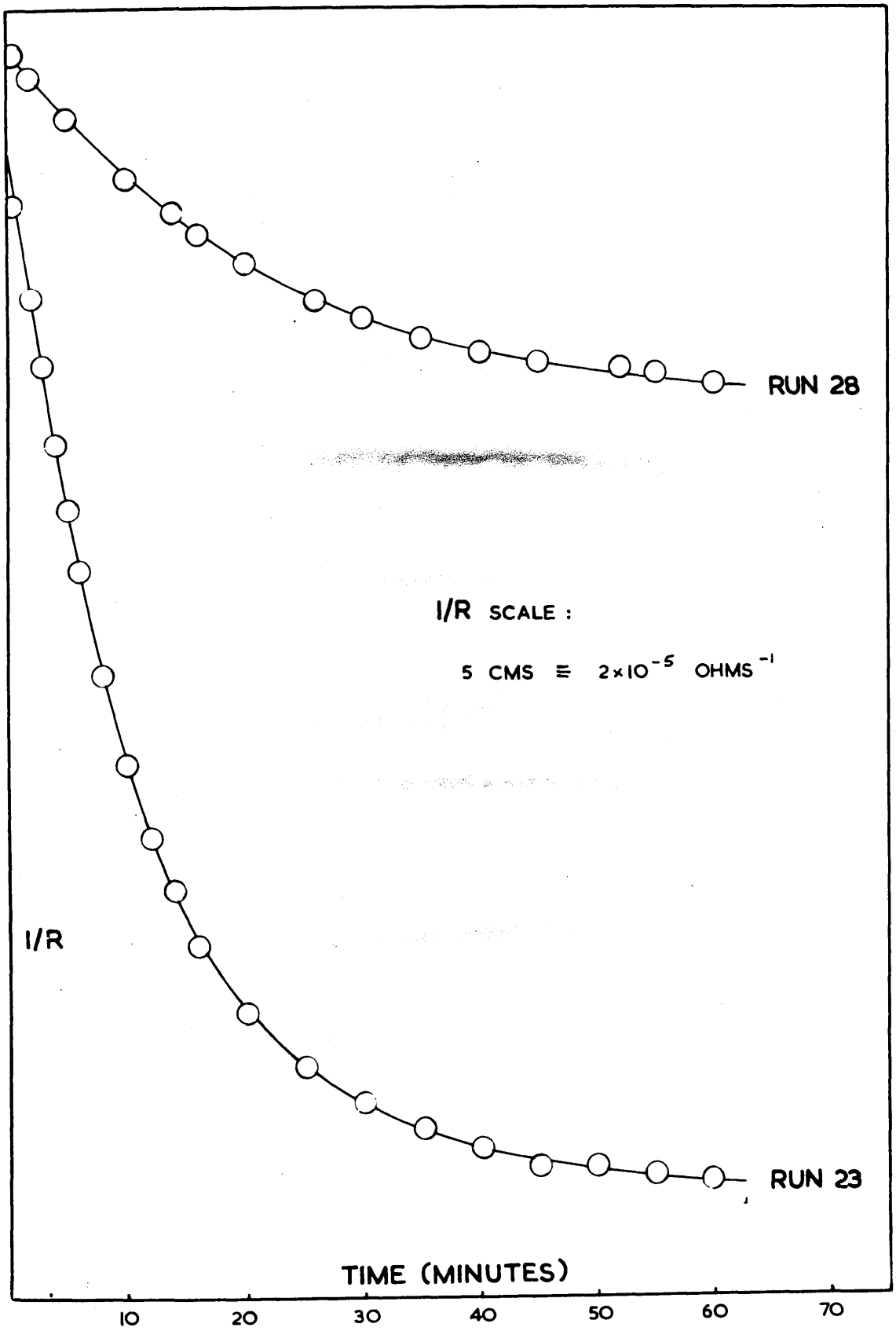
FIGURE 4


RUN 17
RUN 15
RUN 19
1/R
1/R SCALE :
5 CMS. ≡ 2 × 10^5 OHMS^-1
TIME (MINUTES)
10
20
30
40
50
60
70

Seeds prepared by rapid precipitation.

If induction periods were due to adsorbed impurities it seemed reasonable to assume that adsorption would take a finite time. Accordingly, several crystallisations were initiated with seed suspensions which had been prepared immediately before use. Silver chromate, precipitated by adding 5 mls. of 0.0058 M silver nitrate solution to 5 mls. of 0.0029 M potassium chromate solution, was collected by centrifuging and washed six times in conductivity water. The seeds were then made up to $\sim$7 mls. and 5mls. of this suspension, which had been left for ten minutes in the thermostat, were used to initiate crystallisation in each experiment. These crystallisations took place with no trace of induction period and on plotting the reciprocal of the resistance against the time in minutes, smooth curves were obtained : one of these, Run 23, is reproduced in figure 5. If one of the above suspensions was stored for one day before being used, the rate of crystallisation was greatly reduced as in Run 28, figure 5 : after six days no crystallisation was induced. These results indicated that the effect causing the induction periods was one which developed as the seeds were aged in aqueous suspensions.

FIGURE 5


RUN 28
I/R SCALE :
5 CMS ≡ 2×10⁻⁵ OHMS⁻¹
I/R
RUN 23
TIME (MINUTES)
10
20
30
40
50
60
70

Seeds prepared by slow precipitation.

Crystals of good uniformity were prepared by the slow simultaneous addition of 0.06 M silver nitrate and 0.03 M potassium chromate solutions over a period of thirty minutes, to one litre of distilled water, rapidly stirred, and maintained at 40°C. These crystals, consisting of hexagonal needles of length 5 to 10 μ, were dark grey-red and settled out almost as soon as stirring was stopped. The supernatant pale yellow liquid was decanted and after the crystals had been repeatedly washed by decantation, a portion of the suspension was used for inoculation and immediate crystallisation resulted.

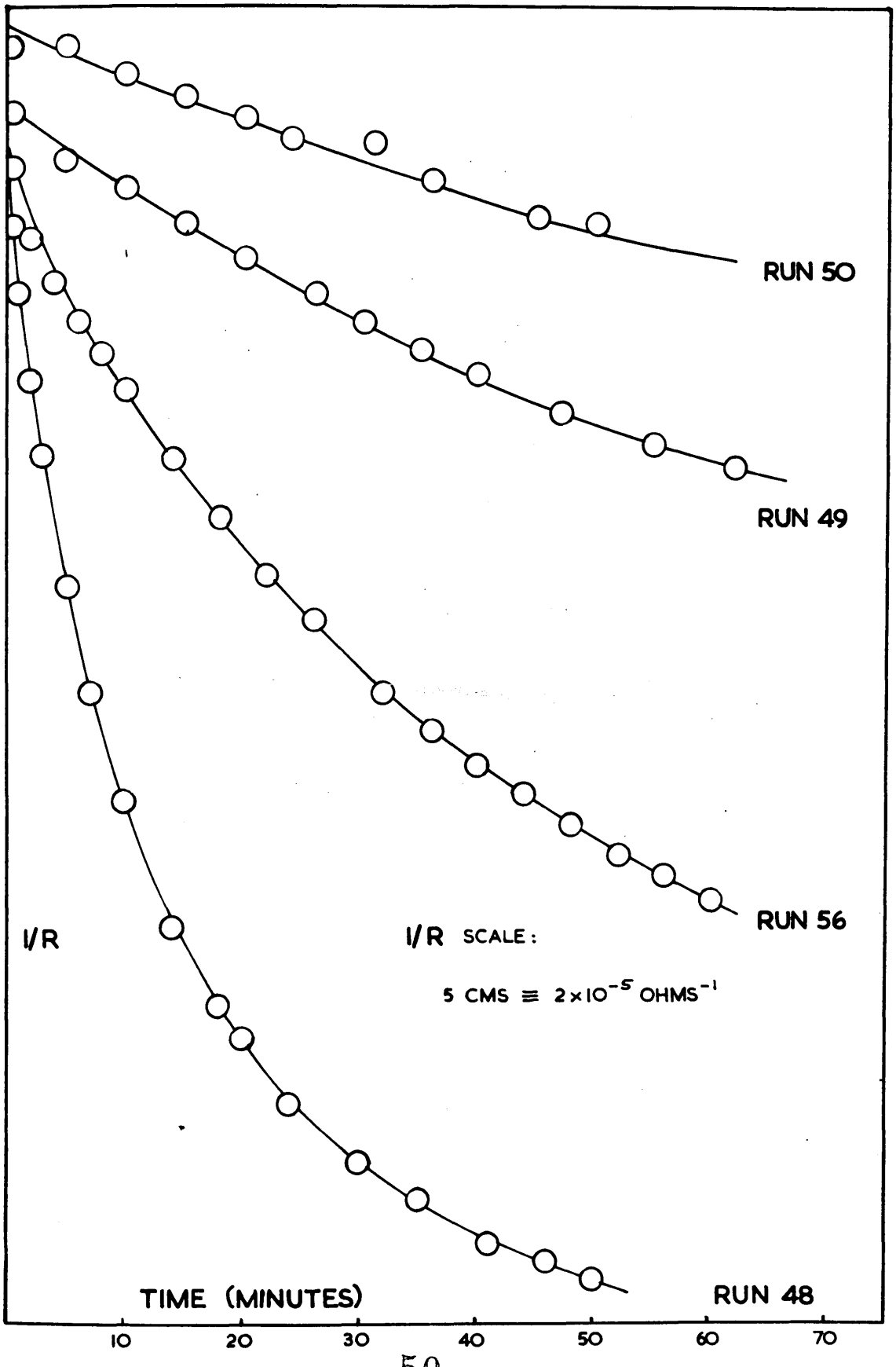
If seeds prepared in this way were stored in predominately alkaline potassium chromate (pH $\sim$ 9) and then washed and used to initiate crystallisation, no induction period was observed but the rate of crystallisation was slow. An attempt to induce or prolong induction periods by storing seeds in dilute acid solution gave inconclusive results.

Seeds stored in organic media.

Crystals prepared by slow precipitation were stored in absolute alcohol and, at first, it seemed very successful

in preventing the adsorption of impurities. After preparation the crystals were washed several times with absolute alcohol and stored as alcohol suspensions for six days. A sample was then withdrawn, washed free from alcohol, prepared as an aqueous suspension, equilibrated for 15 minutes in the thermostat and a measured volume was used to inoculate a supersaturated solution. No trace of induction period was detected in the growth curve (Run 48, figure 6). A series of experiments was then carried out using similar volumes of the aqueous suspension prepared for Run 48. Although no appreciable induction period developed in the course of these experiments the rate of crystallisation fell off (Run 49, figure 6) until, after nine days, the amount of crystallisation was negligible as shown in Run 50, figure 6. It was noted that a considerable amount of air was occluded by seeds from alcohol suspensions, during the first washing, and that, if this was not removed by thorough and repeated wetting, the ability of the seeds to produce a reasonable rate and amount of crystallisation was seriously impaired. After about a month, however, seeds stored in alcohol, washed and used immediately, produced reduced crystallisation rates (Run 56, figure 6) and after five months no crystallisation could be detected on inoculation with alcohol-stored seed suspensions. It appeared that

FIGURE 6


RUN 50
RUN 49
RUN 56
RUN 48
I/R
I/R SCALE:
5 CMS ≡ 2×10⁻⁵ OHMS⁻¹
TIME (MINUTES)
10
20
30
40
50
60
70

absolute alcohol delayed, but did not prevent, the formation of induction periods.

Acetone was found to be more suitable as a storing medium and acetone seed suspensions were used in subsequent crystal growth experiments. The acetone seed suspensions were prepared from crystals obtained by slow precipitation. They were stored in Pyrex bottles at 25^{0}C and made up as aqueous suspensions (page 52) before use. These crystals retained their activity for at least a month and were more easily wetted than those stored in alcohol.

An attempt to use seeds which had been dried and stored in vacuo was unsuccessful because of subsequent wetting difficulties.

4. The Rate of Crystal Growth.

When seed crystals were prepared immediately before use the adverse effects of hydrolysis were avoided but it is likely that the surface area of the seeds would be a very variable factor. It was necessary to conduct experiments using known concentrations of the same seed suspension to demonstrate the reproducibility of the results and to study the crystal growth at various initial ionic ratios

$[Ag^+]/[CrO_4^=]$ so that the kinetics of the process could be established with a greater degree of certainty.

Determination of seed concentration.

12 mls. samples of acetone suspension H were centrifuged to remove the acetone and the crystals were washed six times with conductivity water. Finally, 4 mls. of conductivity water were added to the seeds. 1 ml. of this aqueous suspension was used for inoculation and the concentration of the suspension was determined directly by filtering a known volume through a small weighed sintered glass filter beaker and drying to constant weight at 110-120°C.[54] Using a Stanton semi-micro balance, the determinations of seed concentrations used in the experiments (70, 71, 72) agreed to within 2% and the value was 49mgs./ml.

pH experiments.

The effect of pH variation on chromate solutions has already been discussed, and to investigate any change in pH in the course of crystal growth, experiments exactly analogous to those done in the conductivity cell were carried out in the pH cell. 150 g. of conductivity water were added to the cell and nitrogen was passed over it. The pH

was followed for 2 to 3 hours until steady and 10 mls. of a dilute silver nitrate solution were added, followed by 10 mls. of a dilute potassium chromate solution. On the addition of 1 ml. of seed suspension, prepared as described from suspension H, the pH remained constant to within ±0.01 units for at least 30 minutes. The pH was determined at the end of each crystal growth experiment so that the chromate ion concentration could be corrected for the presence of $HCrO_4^-$ ions.

Crystal growth at equivalent concentrations.

The experimental procedure was the same as that described on page 42 and the results are summarised in Table 2. Variation in the rate of stirring the cell solution from 300 to 800 revs./min. did not affect the rate of growth. The typical smooth curves obtained on plotting 1/R against the time in minutes, shown in figure 6 for Runs 70 and 71, demonstrate the reproducibility of experiments in which the same concentration of seed is used. The low degree of scatter in the recorded resistance readings is shown in the time plots of 1/R for Run 71 in which all the resistance readings are plotted. In the time plots of 1/R for the other experiments summarised in Table 2, only the

TABLE 2

Run	pH	Seed susp.	Initial concentrations $[Ag^+]x10^4$ moles/l.	$[CrO_4^=]x10^4$ moles/l.	$[Ag^+]^2[CrO_4^=]x10^{12}$
23	7.3	A	2.25	0.98	4.96
48	7.3	C	2.21	0.96	4.69
57	7.2	F	2.24	0.93	4.68
70	7.6	H	2.26	1.02	5.23
71	7.6	H	2.26	1.02	5.23

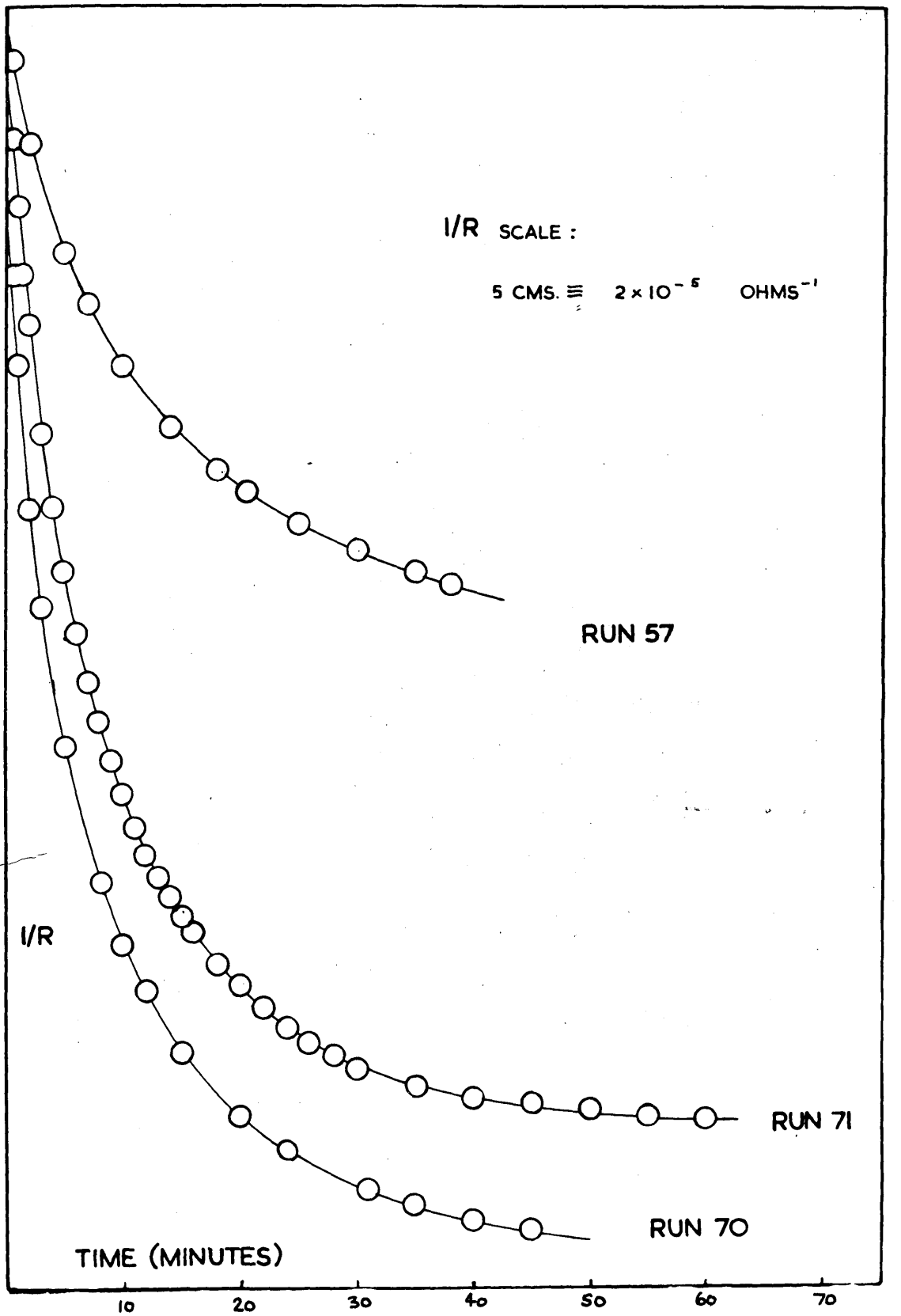
A : Seeds prepared by fast precipitation

C : Seeds stored as alcohol suspension

F : Seeds stored as acetone suspension

H : Seeds stored as acetone suspension.

FIGURE 7


I/R SCALE :
5 CMS. ≡ 2 × 10⁻⁵ OHMS⁻¹
RUN 57
RUN 71
RUN 70
I/R
TIME (MINUTES)
10
20
30
40
50
60
70

resistance readings at five minute intervals are plotted in figures 5, 6, and 7.

From the pH value of the cell solution at the end of each experiment and using the methods described previously, the ratio

$$\alpha = [HCrO_4^-]/[CrO_4^=] = \{H^+\} f_2/f_1 k_a$$

was calculated. Assuming that the electrolytes are completely dissociated at these low concentrations, the observed specific conductivity at any instant may be written

$$\kappa_{obs} = \kappa_{CrO_4^=} + \kappa_{HCrO_4^-} + \kappa_{Ag^+} + \kappa_{H^+} + \kappa_{OH^-} + \kappa_{K^+} + \kappa_{NO_3^-} \quad ..(16)$$

The last four terms on the right hand side of equation (16) remain constant throughout the crystallisation and the change in conductivity $\Delta\kappa_{obs}$, during the experiment is given by

$$10^3 \Delta\kappa_{obs} = \left(2\Lambda_{\frac{1}{2}\ CrO_4^=} + \alpha\Lambda_{HCrO_4^-}\right)\Delta[CrO_4^=] + \Lambda_{Ag}.\Delta[Ag^+] \quad ..(17)$$

in which $\Delta[CrO_4^=]$ and $\Delta[Ag^+]$ represent respectively the decrease in the ionic concentrations of the $CrO_4^=$ and Ag^+ ions in the solution. The electroneutrality expression is

$$2[CrO_4^=] + [HCrO_4^-] + [NO_3^-] + [OH^-] = [Ag^+] + [K^+] + [H^+] \quad ..(18)$$

If $[Ag^+]/[CrO_4^=] = 2/1$, then $[NO_3^-] = [K^+]$, and from equation (18),

$$\Delta[CrO_4^=] = \Delta[Ag^+]/(2 + \alpha) \quad \ldots\ldots\ldots (19)$$

Substituting (19) in (17),

$$\Delta[Ag^+] = \frac{10^3 \Delta\kappa_{obs}(2 + \alpha)}{2\Lambda_{\frac{1}{2} Ag_2CrO_4} + \alpha \Lambda_{AgHCrO_4}} \quad \ldots (20)$$

$\Lambda_{\frac{1}{2} Ag_2CrO_4}$ and Λ_{AgHCrO_4} were obtained from the corresponding Onsager equations (page 34) and the values of $\Delta[CrO_4^=]$ and $\Delta[Ag^+]$ were calculated for the experiments summarised in Table 2.

The rate of fall of conductivity at any instant, and hence the rate of crystallisation, was determined by measuring the slope of the 1/R - time curve. A Perspex sheet on which was scratched a fine straight line was found to be useful for this purpose. The initial rate of crystallisation was obtained by applying the short extrapolation of growth curve to zero time. The difference between the initial and subsequent values of 1/R was used to calculate the amount of silver chromate precipitated at any instant from equations (19) and (20). The corresponding rates were obtained by measuring the slopes of the 1/R - time

curves at these points and correcting for $\Delta[HCrO_4^-]$. Since the total amount of silver chromate precipitated during the experiments only amounted to 3-5 % of the total weight of seed present, changes in the surface area of the seeds due to deposition, could be neglected.

Detailed analyses of all the experiments of Table 2 are given in Tables 3 and 4. When the rate of crystal growth of silver chromate, -dm/dt, is plotted against $(\sqrt[3]{I.P.} - \sqrt[3]{K_s})^3$, where I.P. is the ionic product $[Ag^+]^2[CrO_4^=]$ at time t and K_s is the solubility product of silver chromate, good straight lines passing through the origin are obtained : these are shown in figures 8 and 9. The expression

$$-dm/dt = K (\sqrt[3]{I.P.} - \sqrt[3]{K_s})^3,$$

can therefore be used to represent the kinetics of growth of silver chromate from supersaturated solutions containing equivalent ionic concentrations of silver and chromate. K will be dependent on surface area as is shown by the reproducibility of experiments 70 and 71.

Crystal growth at non-equivalent concentrations.

In these experiments the equations (19) and (20) will still hold since, although the initial ionic ratio

TABLE 3

TABLE 3

$\frac{1}{R}.10^3$	$[Ag^+].10^4$ moles/l.	$[CrO_4^=].10^4$ moles/l.	I.P.x10^{12}	$(\sqrt[3]{I.P.})x10^4$	$(\sqrt[3]{I.P.}-\sqrt[3]{K_s})$ x 10^4	$(\sqrt[3]{I.P.}-\sqrt[3]{K_s})^3$ x 10^{15}	$-\frac{\Delta 1/R}{\Delta t}.10^6$	$-\frac{dm}{dt}.10^6$
Run 23:	$\alpha=0.15$;	$\Delta[Ag^+]=0.04x10^{-4}$;	$\Delta[CrO_4^=]=0.021x10^{-4}$.					
1.048	2.25	0.980	4.96	1.71	0.31	29.8	9.6	2.02
1.038	2.21	0.959	4.68	1.67	0.27	19.7	5.9	1.24
1.028	2.17	0.938	4.42	1.64	0.24	13.8	4.4	0.924
1.018	2.12	0.917	4.12	1.60	0.20	8.0	3.15	0.662
1.008	2.08	0.896	3.88	1.57	0.17	5.0	2.25	0.473
0.998	2.03	0.875	3.61	1.53	0.13	2.2	1.3	0.273
Run 48:	$\alpha=0.15$;	$\Delta[Ag^+]=0.03x10^{-4}$;	$\Delta[CrO_4^=]=0.012x10^{-4}$.					
1.696	2.21	0.961	4.69	1.67	0.27	19.7	5.66	0.679
1.686	2.18	0.949	4.51	1.65	0.25	15.6	5.04	0.605
1.676	2.15	0.937	4.33	1.63	0.23	12.2	3.93	0.472
1.666	2.13	0.925	4.19	1.61	0.21	9.3	2.87	0.344
1.656	2.10	0.913	4.03	1.59	0.19	6.9	2.2	0.264
1.646	2.07	0.901	3.86	1.57	0.17	4.9	1.4	0.168
Run 57:	$\alpha=0.203$;	$\Delta[Ag^+]=0.05x10^{-4}$;	$\Delta[CrO_4^=]=0.023x10^{-4}$.					
0.938	2.24	0.930	4.68	1.67	0.27	19.6	4.2	0.966
0.928	2.19	0.907	4.36	1.63	0.234	12.8	2.6	0.598
0.918	2.14	0.884	4.06	1.595	0.195	7.4	1.7	0.391
0.908	2.09	0.861	3.78	1.56	0.16	4.1	1.0	0.230

TABLE 4

TABLE 4

$\frac{1}{R}.10^4$	$[Ag^+]x10^4$ moles/l.	$[CrO_4^=]x10^4$ moles/l.	I.P.$x10^{12}$	$(\sqrt[3]{I.P.})x10^4$	$(\sqrt[3]{I.P.}-\sqrt[3]{K_s})$ x 10^4	$(\sqrt[3]{I.P.}-\sqrt[3]{K_s})^3$ x 10^{14}	$-\frac{\Delta 1/R}{\Delta t}.10^6$	$-\frac{dm}{dt}.10^6$
Run 70:	$\alpha=0.09$;	$\Delta[Ag^+]=0.05x10^{-4}$;	$\Delta[CrO_4^=]=0.024x10^{-4}$.					
9.30	2.26	1.037	5.30	1.74	0.34	4.07		
9.20	2.21	1.013	4.95	1.71	0.31	2.84	11	2.64
9.10	2.16	0.989	4.61	1.67	0.27	1.88	7.5	1.80
9.00	2.11	0.965	4.30	1.63	0.23	1.20	4.8	1.15
8.90	2.06	0.941	3.99	1.59	0.19	0.70	3.2	0.77
8.80	2.015	0.917	3.72	1.55	0.15	0.35	2.0	0.48
Run 71:	$\alpha=0.09$;	$\Delta[Ag^+]=0.05x10^{-4}$;	$\Delta[CrO_4^=]=0.024x10^{-4}$.					
9.52	2.26	1.037	5.30	1.74	0.34	4.07		
9.42	2.21	1.013	4.95	1.71	0.31	2.84	13	3.12
9.32	2.16	0.989	4.61	1.67	0.27	1.88	7.4	1.78
9.22	2.11	0.965	4.30	1.63	0.23	1.20	4.9	1.18
9.12	2.06	0.941	3.99	1.59	0.19	0.70	3.5	0.84
9.02	2.015	0.917	3.72	1.55	0.15	0.35	2.3	0.55
8.92	1.97	0.893	3.47	1.52	0.12	0.15	1.0	0.24

FIGURE 8

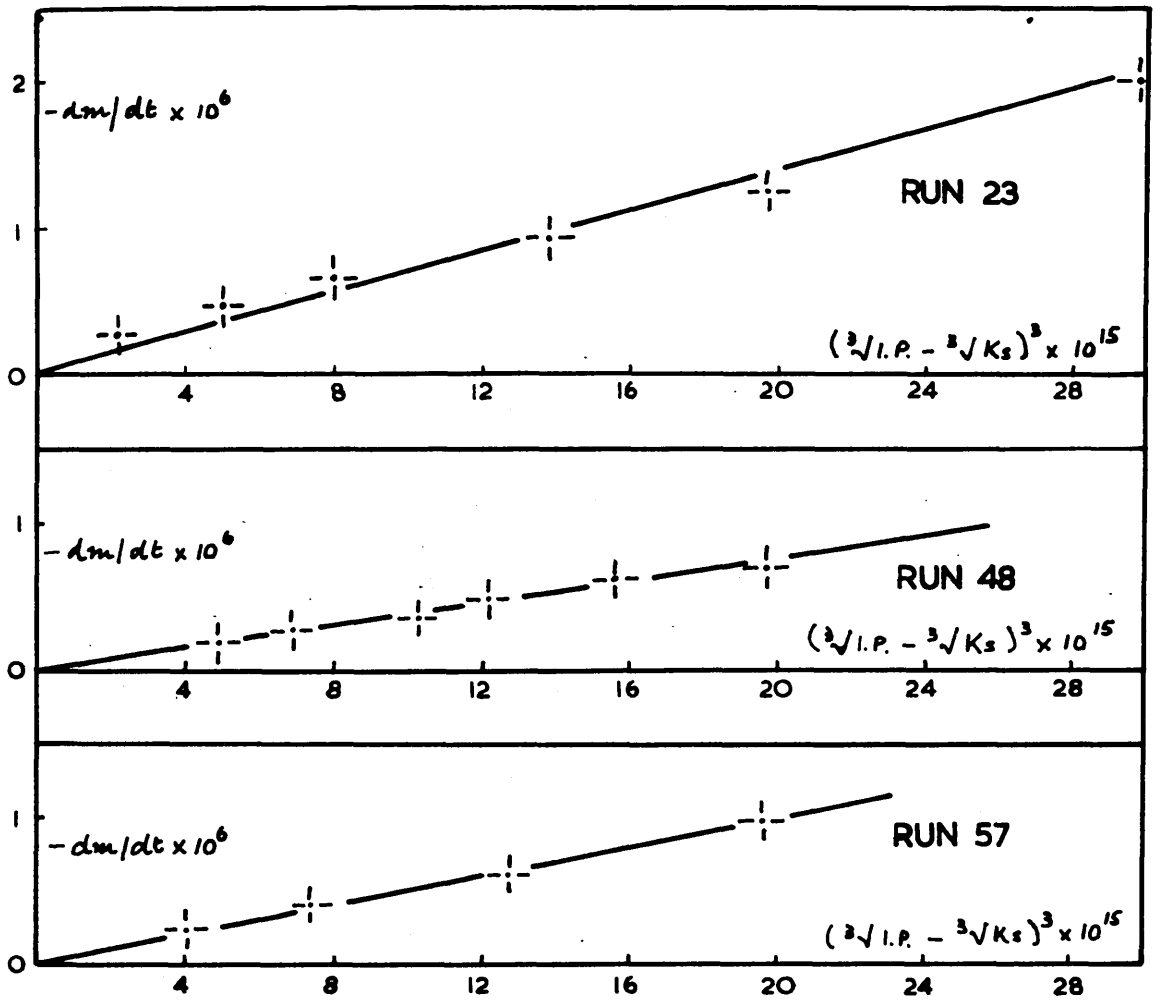
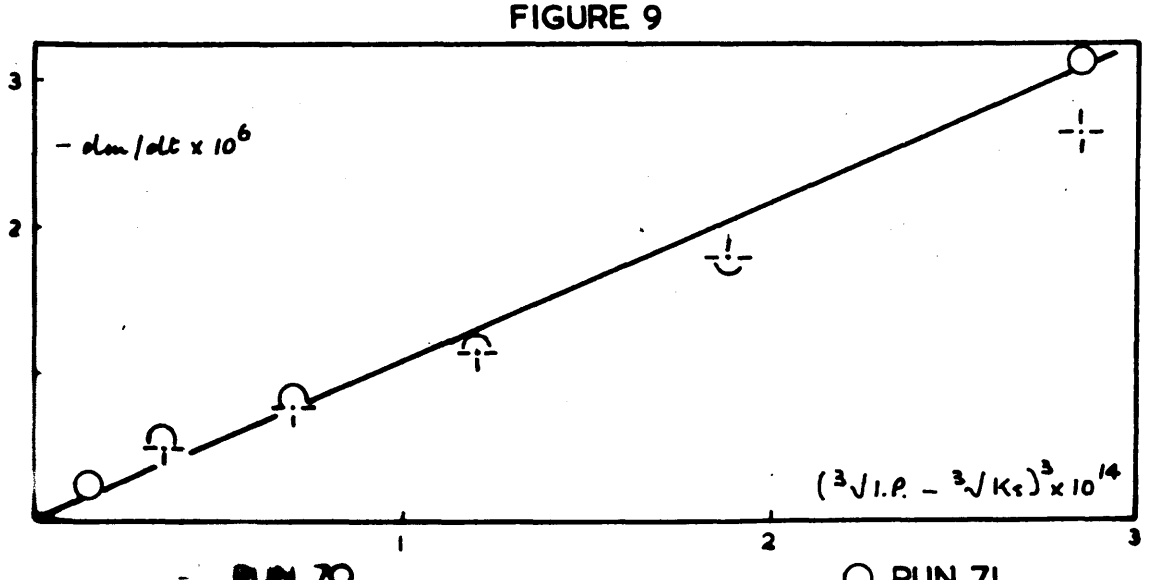


FIGURE 9



$[Ag^+]/[CrO_4^=] \neq 2/1$ and, therefore, $[K^+] \neq [NO_3^-]$, both concentrations may be assumed to be constant during the experiment. The results of experiments at various initial ionic concentrations of silver and chromate are summarised in Table 5 and detailed analyses are given in Table 6. The plots of $-dm/dt$ against $(\sqrt[3]{I.P.} - \sqrt[3]{K_s})^3$ are shown in figure 10.

The growth process may also be analysed in terms of N, the number of moles per litre to be deposited before equilibrium is reached, and N is given by the relationship

$$([Ag^+] - 2N)^2([CrO_4^=] - N)\, f_1 f_2 = 2.44 \times 10^{-12}.$$

It was found that whatever the initial ionic ratio $[Ag^+]/[CrO_4^=]$, the crystallisation obeyed the equation

$$-dm/dt = K' N^3 \quad \ldots\ldots\ldots (21)$$

where m = molar concentration of silver chromate and K' is a constant. Experiments 70, 71 and 72 have been calculated in this way and N values are given in Table 7. The linear plot of $-dm/dt$ against N^3 in figure 11 may be compared with the linear plots of $-dm/dt$ against $(\sqrt[3]{I.P.} - \sqrt[3]{K_s})^3$ for the same experiments in figures 9 and 10.

TABLE 5

Run	pH	Seed susp.	Initial concentrations $[Ag^+]x10^4$ moles/l.	$[CrO_4^=]x10^4$ moles/l.	$[Ag^+]^2[CrO_4^=]$ x 10^{12}
58	7.5	F	3.60	0.41	5.31
59	7.7	F	1.42	2.68	5.40
72	8	H	1.42	2.74	5.52

$\frac{1}{T}\cdot 10^3$	$[\Delta s^+]\cdot 10^4$ moles/l.	$[\sigma r o_4^=]\cdot 10^4$ moles/l.	$I.P.\times 10^{-12}$	$(\sqrt{\ldots})$
Run 25:	$\alpha=0.1$;	$\Delta[\Delta s^+]=0.05\times 10^{-4}$;	$\Delta[\sigma r o_4^=]=0.022\times 10^{-}$	
0.920	3.60	0.410	5.31	1.745
0.910	3.55	0.388	4.89	1.725
0.900	3.50	0.366	4.48	1.69
0.890	3.45	0.344	4.09	1.66
0.880	3.40	0.322	3.72	1.63
Run 23:	$\alpha=0.06$;	$\Delta[\Delta s^+]=0.047\times 10^{-4}$;	$\Delta[\sigma r o_4^=]=0.025\times 10^{-}$	
1.58	1.42	2.68	5.40	1.72
1.57	1.37	2.66	4.99	1.71
1.56	1.35	2.65	4.85	1.69
1.55	1.28	2.61	4.28	1.65
1.54	1.25	2.59	3.92	1.63
Run 22:	$\alpha=0.037$;	$\Delta[\Delta s^+]=0.049\times 10^{-4}$;	$\Delta[\sigma r o_4^=]=0.024\times 10^{}$	
1.58	1.42	2.74	5.52	1.77
1.57	1.37	2.71	5.10	1.72
1.56	1.32	2.69	4.70	1.68
1.55	1.27	2.67	4.32	1.63
1.54	1.22	2.64	3.96	1.58
1.53	1.18	2.62	3.61	1.54

TABLE 6

$\frac{1}{R}.10^3$	$[Ag^+].10^4$ moles/l.	$[CrO_4^=].10^4$ moles/l.	I.P.x10^{12}	$(\sqrt[3]{I.P.})x10^4$	$(\sqrt[3]{I.P.}-\sqrt[3]{K_s})$ x 10^4	$(\sqrt[3]{I.P.}-\sqrt[3]{K_s})^3$ x 10^{14}	$-\frac{\Delta 1/R}{\Delta t}.10^6$	$-\frac{dm}{dt}.10^6$
Run 58: $\alpha=0.1$; $\Delta[Ag^+]=0.05x10^{-4}$; $\Delta[CrO_4^=]=0.022x10^{-4}$.								
0.920	3.60	0.410	5.31	1.745	0.345	4.11	9.6	2.11
0.910	3.55	0.388	4.89	1.76	0.36	2.70	6.2	1.36
0.900	3.50	0.366	4.48	1.65	0.25	1.56	3.6	0.792
0.890	3.45	0.344	4.09	1.60	0.20	0.80	1.8	0.396
0.880	3.40	0.322	3.72	1.55	0.15	0.34	0.6	0.132
Run 59: $\alpha=0.06$; $\Delta[Ag^+]=0.047x10^{-4}$; $\Delta[CrO_4^=]=0.023x10^{-4}$.								
1.58	1.42	2.68	5.40	1.75	0.35	4.29	11.0	2.53
1.57	1.37	2.66	4.99	1.71	0.31	2.98	7.6	1.75
1.56	1.33	2.63	4.65	1.67	0.27	1.97	4.5	1.04
1.55	1.28	2.61	4.28	1.63	0.23	1.22	2.3	0.529
1.54	1.23	2.59	3.92	1.58	0.18	0.60	0.9	0.207
Run 72: $\alpha=0.037$; $\Delta[Ag^+]=0.049x10^{-4}$; $\Delta[CrO_4^=]=0.024x10^{-4}$.								
1.58	1.42	2.74	5.52	1.77	0.37	4.94	11.8	2.83
1.57	1.37	2.71	5.10	1.72	0.32	3.34	7.0	1.68
1.56	1.32	2.69	4.70	1.68	0.28	2.08	4.4	1.06
1.55	1.27	2.67	4.32	1.63	0.23	1.20	3.0	0.720
1.54	1.22	2.64	3.96	1.58	0.18	0.60	1.7	0.408
1.53	1.18	2.62	3.61	1.54	0.14	0.25	0.45	0.108

TABLE 7

$N \times 10^4$ moles/l.	$N^3 \times 10^{14}$	$-\frac{dm}{dt} \times 10^6$	
		(70)	(71)
	Runs 70, 71		
0.208	8.999		
0.184	6.230	2.64	3.12
0.160	4.096	1.80	1.78
0.136	2.515	1.15	1.18
0.112	1.405	0.77	0.84
0.088	0.682	0.48	0.55
0.064	0.262		0.24
	Run 72		
0.175	5.38	2.83	
0.151	3.44	1.68	
0.127	2.05	1.06	
0.103	1.09	0.72	
0.079	0.49	0.408	
0.055	0.17	0.108	

FIGURE 10

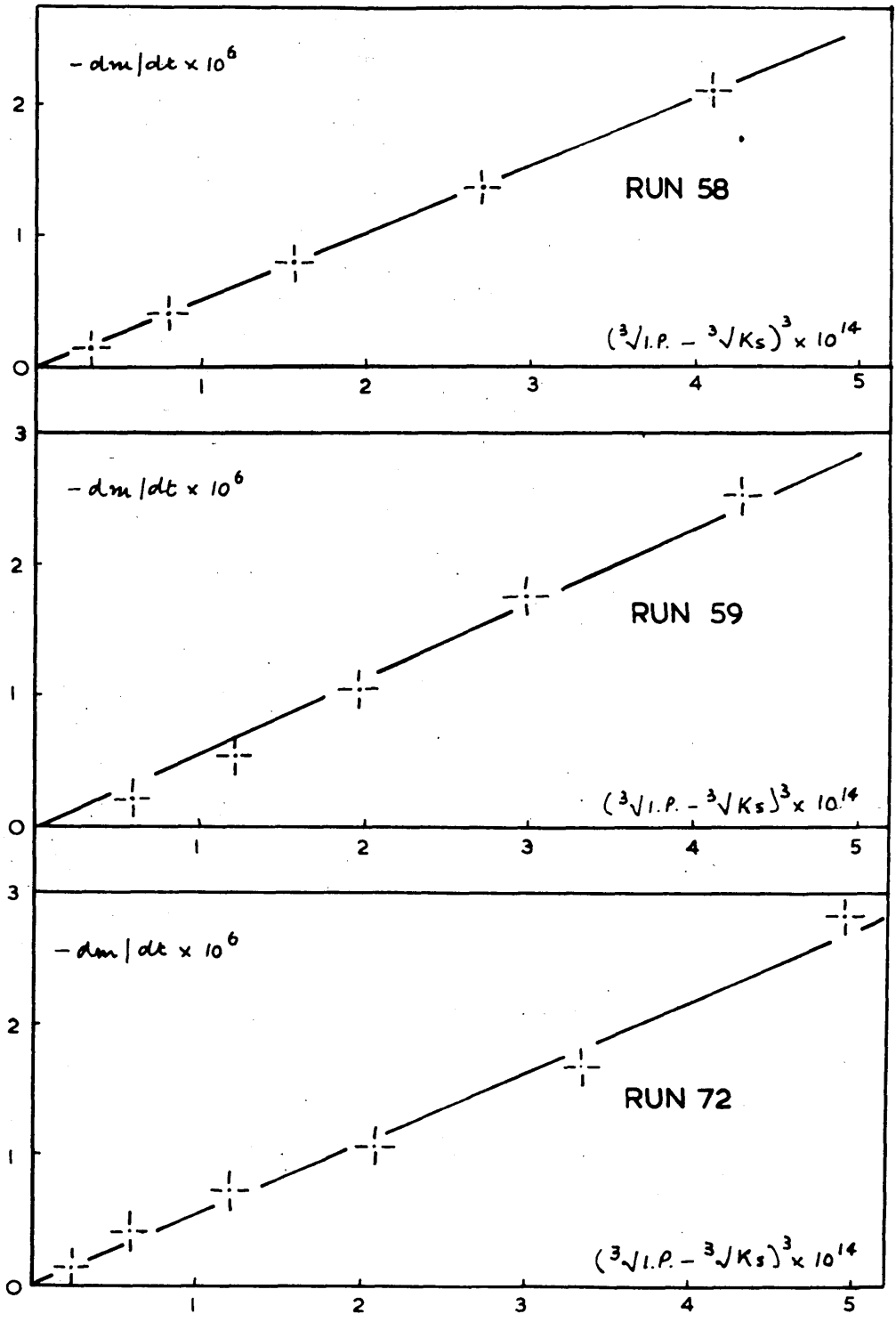
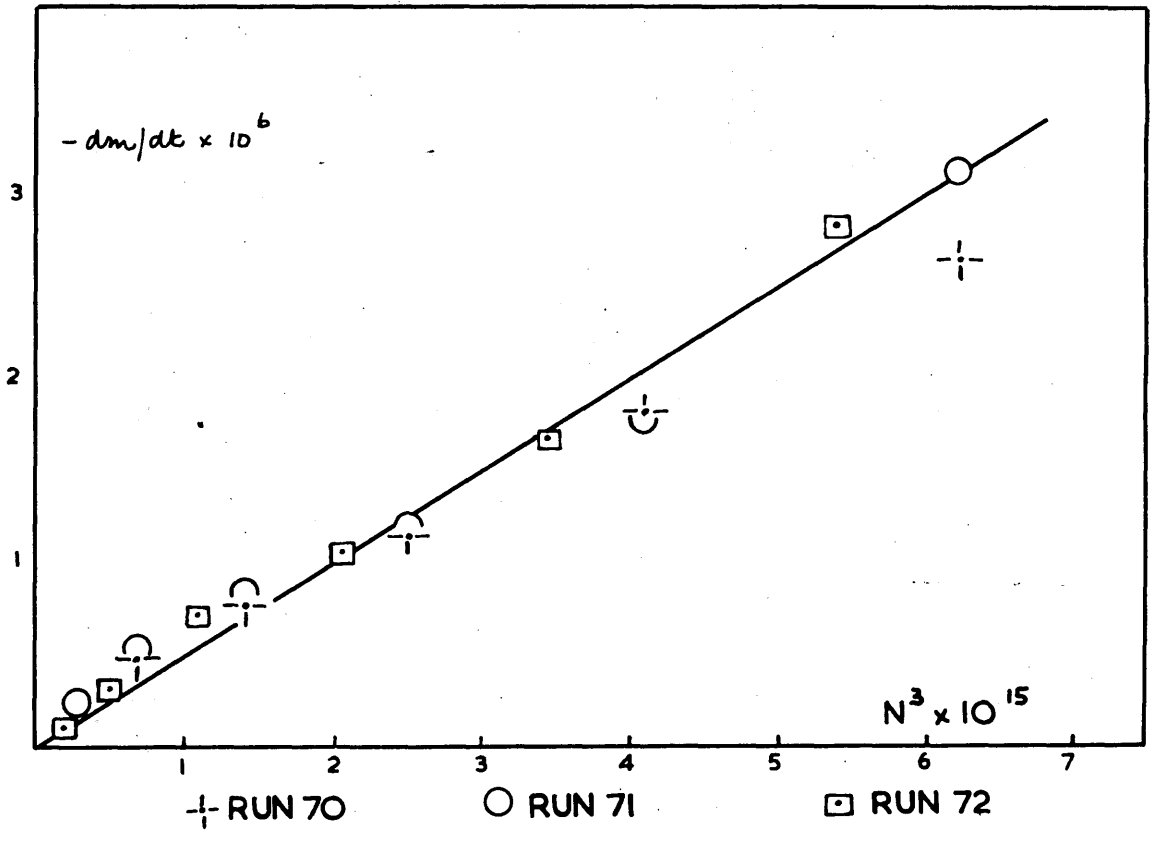

$-dm/dt \times 10^6$
RUN 58
$(\sqrt[3]{I.P.} - \sqrt[3]{Ks})^3 \times 10^{14}$
$-dm/dt \times 10^6$
RUN 59
$(\sqrt[3]{I.P.} - \sqrt[3]{Ks})^3 \times 10^{14}$
$-dm/dt \times 10^6$
RUN 72
$(\sqrt[3]{I.P.} - \sqrt[3]{Ks})^3 \times 10^{14}$

FIGURE 11



DISCUSSION

Although the experiments of van Hook [45] were complicated by the use of supersaturated solutions whose concentration was greater than the critical concentration, his discovery that aged aqueous suspensions of silver chromate did not cause immediate crystallisation has been confirmed. The present work has also shown that precipitated silver chromate seed crystals, which were not in prolonged contact with water or recrystallised from aqueous solution, will grow immediately when used to inoculate supersaturated solutions. Since it had been shown[28] that induction periods could be induced in the growth of silver chloride by storing seed crystals in contact with solutions of easily adsorbed substances, it was thought probable that silver chromate crystals became poisoned on ageing as aqueous suspensions. The ready hydrolysis of chromate solutions pointed to the adsorption of hydrolysis products - possibly $HCrO_4^-$ ions. It was difficult to prove this conclusively by direct conductimetric investigation owing to the high conductivity of H^+ ions and the solubility of silver chromate in acid

solutions, which made the preparation of suitably buffered solutions over a wide pH range impossible.

In the present work the existence of hydrolysis products has been demonstrated by preserving the activity of precipitated seeds by storing them in media which did not favour hydrolysis. It was also found that the induction periods observed in the growth of recrystallised seeds could not be removed by washing as easily as those induced in the silver chloride experiments. The recrystallised silver chromate seeds had to be repeatedly washed in hot water before any growth could be detected. On boiling the aqueous seed suspensions before inoculation to expose a fresh crystal surface, the induction period was further reduced but not entirely removed. The $HCrO_4^-$ ions would be likely to be more compatible with the lattice ions Ag^+ and $CrO_4^=$ than for example eosin and other adsorbates are with Ag^+ and Cl^- ions. The $HCrO_4^-$ ions may be incorporated to some extent into the silver chromate crystal lattice, while the adsorbates will remain on the crystal surface and be removed by washing when the seeds are added to the supersaturated solutions.

In studying the influence of gelatine on the precipitation of silver chromate in solutions of varying pH,

Bolam and MacKenzie[55] found that gelatine was more effective in inhibiting precipitation after being treated with acetic acid solutions. The acid gelatine was added to the potassium chromate solution used in precipitating silver chromate from silver nitrate and no difference in the colour of the chromate solution could be detected except on the addition of very acid gelatine. Bolam and MacKenzie considered, therefore, that the enhanced solubility of silver chromate in the presence of acid gelatine was not due to dichromate formation. Experiments in which acetic acid solutions alone were used in place of acid gelatine also showed inhibited precipitation but the effect was less marked. Bolam and MacKenzie suggested that increased acidity produced some change in the gelatine itself which improved its inhibiting efficiency. In a second paper, Bolam and Donaldson[56] found that the inhibiting action of the gelatine had an optimum value at pH = 5.0.

When these results are compared with those obtained in the present work, the inhibiting action of acid solution and the increased efficiency of acid gelatine in preventing precipitation of silver chromate might be attributed to the formation of $HCrO_4^-$ ions. At the 'optimum pH' of 5.0 found by Bolam and Donaldson, appreciable concentrations of $HCrO_4^-$ will be present.

The third order rate equations obtained in the present work for the growth of silver chromate crystals from supersaturated solutions can be interpreted, in terms of the adsorbed layer theory of Davies[17], by postulating that crystallisation takes place through the simultaneous arrival at the growth site of two silver ions and one chromate ion. The hydrated ions of the adsorbed layer are subsequently dehydrated and pass into the crystal lattice.

The concentrations of silver and chromate ions available at the surface are respectively

$$K''a[Ag^+] \qquad \text{and} \qquad K''a[CrO_4^=] ,$$

where K'' is a constant and a is the surface area of seed crystals. In the adsorbed monolayer, the concentrations of silver and chromate are equivalent and stationary, and if S is the solubility of silver chromate, the concentrations of Ag^+ and $CrO_4^=$ ions available for growth are

$$K''a([Ag^+] - 2S) \quad \text{and} \quad K''a([CrO_4^=] - S)$$

since there are twice as many silver as chromate ions available for growth. The rate of growth is given by

$$-dm/dt = K''a([Ag^+]- 2S)^2([CrO_4^=]- S), \quad \ldots\ldots (22)$$

a third order function of the supersaturation. Owing to the existence of $HCrO_4^-$ ions in all the supersaturated solutions of silver chromate, $2[Ag^+]$ was not exactly equal to $[CrO_4^=]$ even in solutions made from equivalent concentrations of potassium chromate and silver nitrate, and corrections had to be made for this.

In solutions containing non-equivalent concentrations of silver and chromate ions, there exists a potential difference, ψ, between the adsorbed layer and the solution, the sign of ψ depending on the lattice ion in excess. If $2[Ag^+] > [CrO_4^=]$, e is the charge on a proton and k is Boltzmann's constant, the concentrations of silver and chromate ions available at the surface are respectively

$$K_1 a[Ag^+]\exp(-e\psi/kT) \quad \text{and} \quad K_1 a[CrO_4^=]\exp(2e\psi/kT),$$

where K_1 is a constant and a is the surface area of seeds as before. Since the value of ψ is such that twice as many silver as chromate ions reach the surface,

$$[Ag^+] = 2[CrO_4^=]\exp(3e\psi/kT)$$

$$\text{and} \quad \exp(e\psi/kT) = \sqrt[3]{([Ag^+]/2[CrO_4^=])}.$$

The number of silver and chromate ions entering the mono-

layer in unit time is $2S$ and S respectively and the rate of crystal growth

$$-dm/dt = K_1 a \left\{ [Ag^+]\exp(-e\psi/kT) - 2S \right\}^2 \left\{ [CrO_4^=]\exp(2e\psi/kT) - S \right\}$$

$$= K_1 a \left\{ \sqrt[3]{([Ag^+]^2[CrO_4^=])} - \sqrt[3]{K_s} \right\} .$$

$$\text{i.e. } -dm/dt = K_1 a \left(\sqrt[3]{\text{I.P.}} - \sqrt[3]{K_s} \right)^3 \quad \ldots\ldots\ldots\ldots (23)$$

In experiments 70, 71 and 72 , the value of a was constant within experimental error and $K_1 a$ could be replaced by an overall constant K

$$\text{i.e. } -dm/dt = K \left(\sqrt[3]{\text{I.P.}} - \sqrt[3]{K_s} \right)^3 .$$

In figures 9 and 10 in which $-dm/dt$ was plotted against $\left(\sqrt[3]{\text{I.P.}} - \sqrt[3]{K_s} \right)^3$ for these experiments, K varied with ionic ratio having a maximum when $[Ag^+]/[CrO_4^=] \simeq 2/1$, whereas in figure 11 K', derived from considerations of the amount of Ag^+ and $CrO_4^=$ ions to be deposited before equilibrium is reached (equation 21), was constant. A similar result was obtained in silver chloride experiments[17,23], the decrease in K being a measure of the decrease in available growth sites due to adsorption of the lattice ion in excess at the monolayer.

PART 2

DISSOLUTION OF SILVER CHLORIDE AND SILVER CHROMATE

INTRODUCTION

The data obtained from the study of many dissolution reactions laid the foundation of Nernst's diffusion theory of heterogeneous reactions. Noyes and Whitney[20] found that the dissolution of rods of benzoic acid and lead chloride followed the first order rate equation

$$-dc/dt = k (c_o - c) ,$$

where c is the concentration of the solution at time t and c_o is the solubility, and suggested that a saturated layer was rapidly formed at the solid-solution interface and that the observed rate then depended on the rate at which molecules diffused from the layer to the bulk of the solution. Similar results were obtained by Bruner and St. Tolloczko[21] who showed that the rate constant was proportional to the apparent surface area of the solute.

Nernst[22] extended these views to dissolution reactions in which water was not the solvent such as the dissolution of metals in acids. In formulating his theory he assumed that chemical processes at the surface were much

faster than transport processes and that, in a well-stirred system, the concentration gradient was confined to a thin layer of thickness δ , adhering to the solid, in which the concentration varied linearly with distance measured normal to the solid surface. There was considerable support for Nernst's theory but many valid criticisms have also been made.

A diffusion-controlled reaction should be influenced by the efficiency with which the system is stirred and this will depend on the rate of stirring and the geometry of the system. Several workers[57-63] have found that the rate constants (k) of dissolution reactions depend on the rate of stirring as follows:

$$k \propto (\text{revs. per min.})^{a}.$$

Values of a varied from 0.56 to 1. However, for the dissolution of some metals in acids[64] and of glass in alkali[65], the rate of reaction was observed to be independent of the rate of stirring.

Nernst[22] assumed that δ was approximately the same in reactions of quite different chemical character provided the type and rate of stirring was the same. In support of this Brunner[58] has shown that the δ value (3×10^{-3} cms.)

derived from the dissolution of benzoic acid in water can be used to calculate the rate of solution of magnesia in different acids. Also, van Name et al[59,66] showed that the rate of solution of metals in aqueous iodine was the same. Bircumshaw and Riddiford[57] have confirmed the latter results but point out that they are to be expected since the iodine will diffuse at the same rate in all the experiments. The δ values derived by Brunner[58] are considered physically improbable by Moelwyn-Hughes[67]. There is much evidence[68,69] to support the view that in a well-stirred system, fluid motion persists down to much shorter distance than 10^{-3}cms. from the solid surface, and, as Bircumshaw and Riddiford have suggested[70], the linear concentration gradient suggested by Nernst can then only be an approximation: this view has been supported by Levich[71].

The velocity of solution of a solute, if it is a diffusion-controlled process, will depend on the distance through which the solute is transported (δ), the diffusion coefficient of the solute and the viscosity of the solution. In studying the effect of viscosity, van Name and Edgar[59] have shown that bromine attacks metals more rapidly than iodine and several workers have confirmed[61,72-74] that increase in the viscosity of solvent decreases the rate of solution of particular solutes. If δ was constant, the

rate constant k for a given surface area should be proportional to D, the diffusion coefficient of the solute. Experiments on the dissolution of magnesium cylinders in acids[75-77] gave

$$k \propto D^x ,$$

where x varied from 0.66 to 0.75, depending on the experimental conditions of flow.

The effect of temperature on several dissolution reactions[78] has been studied and the values of the activation energy E obtained from the equation

$$\ln k = \ln A - E/RT ,$$

where k is the rate constant at temperature T and A and R are constants. These values were of the order of magnitude expected for the energy of activation for diffusion, but Moelwyn-Hughes[67] has indicated that some heterogeneous reactions which are controlled by chemical processes have similar values. Davies and Nancollas[23] have studied the dissolution of silver chloride seed crystals into water at various temperatures by following the rise in conductivity when the crystals were added to conductivity water. They found that if w_1 g. of seed crystals were reduced to w_2 g.

in the course of the reaction, the rate of solution could be written,

$$\frac{dc}{dt}\left(\frac{w_1}{w_2}\right)^{2/3} = k\,(c_o - c)^n \quad .$$

At 15° and 25°C, n = 3/2 and at 35°C, n = 2.

The restricted field of heterogeneous dissolution reactions considered above are sufficient to indicate the limitations of Nernst's theory. It is evident that not all dissolution experiments are purely diffusion controlled. In those cases where a first order rate equation

$$dc/dt = k\,A\,(c_o - c)$$

was obtained, the thickness of the layer in which the concentration gradient existed would be a function of the viscosity of the solution. The rate of dissolution would depend on the diffusion coefficient of the solute, the solvent used, the efficiency of stirring and the temperature of reaction.

Modern theory suggests that diffusion-controlled heterogeneous reactions and those controlled by chemical processes are the extreme cases and that between these many heterogeneous reactions are intermediate in type. If this is so, a marked change in the experimental conditions of a

particular dissolution reaction might alter the apparent order of the reaction.

In the experiments of Davies and Nancollas[23] in which large numbers of crystals were dissolving simultaneously instead of the single massive block used in other work, special reaction conditions prevailed. The size of each crystal would diminish during the experiment and each would be surrounded by a concentration gradient. Although Davies and Nancollas established that the size of the crystals did not decrease to the extent at which an enhanced solubility would be predicted by the Gibbs-Thomson equation, they recognised that there was an inherent experimental uncertainty in the conductimetric method. They estimated that the average distance between crystals was 7×10^{-2} cms. in their experiments. The concentration gradient surrounding each particle could be a significant fraction of this mean distance between particles and the measured conductance would then cease to give a true representation of concentration : this error might be significant in conditions where c/c_o, the ratio of the momentary concentration to its saturation value, was very much less than unity.

The present work has been undertaken to study the kinetics of the above dissolution reaction when the

experimental conditions are changed. The rate of solution of silver chloride seed crystals into subsaturated solutions of silver chloride has been studied conductimetrically. When subsaturated solutions are used in this way the following experimental advantages are introduced:

1. The weight of seed crystals dissolved in the course of an experiment is negligible compared with the weight added so that the surface area may be assumed constant.

2. The concentrations of the subsaturated solutions can be adjusted so that the initial rates of solution, even with appreciable amounts of added seed crystals, are not too fast and accurate resistance readings are obtained.

3. The concentration gradient prevailing during the dissolution process is decreased and it would seem likely that any effect due to parity in the average distance between particles and the thickness of their diffusion layers would be minimised.

The dissolution of silver chromate seed crystals into subsaturated solutions has also been investigated to extend the study to a salt of higher valence type, but the effect of hydrolysis on this system makes interpretation of results more difficult.

EXPERIMENTAL

The concentrations of subsaturated solutions used in studying the dissolution of silver chloride were such that when 4-6 mgs. of seed crystals were used for inoculation, the initial rates of dissolution were not too fast for accurate measurement.

The increase in conductivity of subsaturated silver chloride solutions on addition of seed crystals was less than one tenth of the decrease in conductivity in silver chromate crystallisation experiments and some modifications were made in the conductivity apparatus so that the smaller changes could be followed accurately. The conductivity cells used in the dissolution work were cells B and E. Fine lines, etched on the cap and base of these cells, were aligned to fix the position of the electrodes before each experiment. The cell constants were 0.06897 for cell B and 0.07800 for cell E. The cell stirrer was supported in a Quickfit stirrer gland which was coupled to the pulley of a stirrer motor by an elastic band. This replaced the pulley shaft and belt previously described (page 14) and

eliminated belt slip. The rate of stirring was measured by a revolution counter connected by rubber tubing to the shaft of the electric motor and clamped in position above the motor. The usual stirring rate of approximately 600 revs./min. was maintained throughout experiments.

Preparation of seed suspensions.

Silver chloride : The silver chloride seed suspensions were prepared as described by Jones[16]. 5 g. of silver chloride precipitated from equivalent solutions of silver nitrate and potassium chloride, were washed by decantation with distilled water and portions of precipitate were boiled for two hours with four litre volumes of distilled water contained in Pyrex beakers covered with clock glasses. The boiling saturated solutions were then filtered through a double layer of large fluted filter papers and collected in Pyrex flasks which were heat insulated with cotton wool: both the filter funnel and the flasks were preheated. The filtrate was stored overnight, the cotton wool was then removed and the solutions were left in darkness for a further 24 hours to come to room temperature. Between 20 and 40 litres of distilled water were treated in this way to prepare each of the silver chloride suspensions used in the present work.

In a darkened laboratory illuminated with red lamps, the crystals which formed when the solutions cooled were collected by decantation and washed several times, first with distilled water and then with conductivity water: each suspension was vigorously shaken and centrifuged. The crystals were finally transferred to a steamed out Pyrex bottle the outside of which was painted black and coated with a layer of paraffin wax. The volume of each suspension was between 50 and 150 mls. and they were allowed to age for about one month.

Microscopic examination of the seed crystals showed that they were rectangular plates or cubes and occurred singly or in small clusters. Several slides were prepared containing samples of suspension and large numbers of crystals were observed. If the crystal size is expressed as the length of side of a crystal, most of the crystals were between 2 and 5μ. The smallest crystal measured was ~1μ and the largest ~ 7μ.

The seed concentration of each suspension was measured as described previously for silver chromate suspensions (page 52) and the values were:

Suspension	A	B	C	D
Concentration (mgs./ml.) ...	1.25	0.65	0.91	3.06

Suspensions were aged and the above seed concentrations were obtained at 25°C. Samples of each of the suspensions C and D were stored at 15°C and at 35°C for use subsequently in temperature coefficient experiments. The seed concentration of each sample of suspension D was measured to avoid sampling errors and the values obtained were 3.06 mgs. per ml. at 15°C and 3.26 mgs. per ml. at 35°C.

Silver chromate. Seed crystals were prepared by rapid precipitation , by adding 20 mls. of 0.002M potassium chromate solution to 20 mls. of 0.004M silver nitrate solution. The crystals were collected by centrifuging and washed three times with distilled water. 2 mls. of conductivity water were then added to the seeds and the suspension was equilibrated in the thermostat for 10 minutes before use.

Experimental procedure.

Silver chloride : 250 g. of conductivity water were placed in cell B or cell E and equilibrated in a rapid stream of carbon dioxide-free air in the oil thermostat as previously described. When the resistance of the water had reached a steady value, 10 mls. of a dilute silver nitrate solution were added, followed 1-2 hours later by 10 mls,

of a dilute potassium chloride solution which was added dropwise over a period of approximately three minutes. In the experiments in which $[Ag^+]/[Cl^-] = 1$, the concentrations of silver and chloride ions in the subsaturated solutions formed in the cell were equal to within 0.1 % and their product corresponded to a subsaturation of about 46 % at 15°C, 30 % at 25°C and 22 % at 35°C.

After about two hours the subsaturated solution came to carbon dioxide and temperature equilibrium. Before use the required seed suspension was vigorously shaken in a stream of nitrogen for 15 minutes, and a homogeneous sample was then added to the cell as a stop-clock was started (see Part 1, page 43). Bridge readings were taken after the first half minute and then at the end of each minute for 20 minutes. As the rate of solution became slower, bridge readings were taken at 2 minute and then at 5 minute intervals for at least an hour.

Silver chromate : Subsaturated solutions of silver chromate were prepared in the conductivity cell as described above. The concentration of the dilute silver nitrate and potassium chromate solutions added to the cell were such that the concentration of silver ions was approximately twice the concentration of chromate ions and the cell

solution was 30-35 % subsaturated.

The seed suspension was prepared immediately before use and 1 ml. was used to inoculate the stable subsaturated solution in the cell. The subsequent change in resistance was followed as described for the silver chloride experiments.

RESULTS

1. Dissolution of Silver Chloride.

The dissolution of silver chloride seed crystals into subsaturated solutions has been studied at 15, 25, and 35°C. At 25°C, the effect of varying several experimental conditions has been investigated so that as complete a picture as possible of the dissolution process might be obtained.

Solubility and mobility values.

The solubility of silver chloride in water at various temperatures has been determined by many workers and a number of different values have been quoted[79]. Using an electrochemical method, Owen[80] has determined the solubility of electrolytic silver chloride in water at temperatures ranging from 5 to 45°C. The value at 25°C (1.334×10^{-5} g.equivs./l.) agrees very well with that found by Davies and Jones[17] by conductimetric measurements (1.337×10^{-5} g.equivs./l.). In the present work the solubility value 1.337×10^{-5} g.equivs./l. was used at 25°C and Owen's values

of 0.840×10^{-5} g.equivs./l. and 2.036×10^{-5} g.equivs./l. were used at 15°C and 35°C respectively.

The amount of silver chloride dissolved at any moment was calculated from the equation :

$$\Delta c = (1000/\Lambda)\,\Delta\kappa$$

which relates Δc, the increase in equivalent concentration of the subsaturated solution to $\Delta\kappa$, the corresponding increase in specific conductivity : Λ is the sum of the ionic conductances of silver and chloride ions, calculated from the appropriate Onsager equations[49]

at 15°C, $\Lambda = \Lambda_o - (0.2237\,\Lambda_o + 46.53)\sqrt{c}$,

at 25°C, $\Lambda = \Lambda_o - (0.2277\,\Lambda_o + 59.86)\sqrt{c}$,

and at 35°C, $\Lambda = \Lambda_o - (0.2322\,\Lambda_o + 74.81)\sqrt{c}$.

Within the experimental error, Λ_{AgCl} could be regarded as constant at each temperature as the solutions investigated were all within a small range of ionic strength. The values employed were

$$\Lambda_{AgCl} = 112.14 \text{ at } 15^\circ\text{C},$$
$$= 137.97 \text{ at } 25^\circ\text{C},$$
$$= 165.44 \text{ at } 35^\circ\text{C},$$

and were calculated using the mobility values

$\Lambda^{o}_{Ag} = 50.90$ [81] ; $\Lambda^{o}_{Cl} = 61.42$ [82] at 15°C,

$\Lambda^{o}_{Ag} = 61.92$ [48] ; $\Lambda^{o}_{Cl} = 76.34$ [48] at 25°C,

and $\Lambda^{o}_{Ag} = 73.32$ [81] ; $\Lambda^{o}_{Cl} = 92.25$ [83] at 35°C.

Experiments at 25°C.

These are summarised in Table 8.

Some typical smooth curves obtained on plotting the reciprocal of the resistance against the time in minutes for experiments at 25°C are plotted in figures 12, 13, 14, and indicate the low degree of scatter in the recorded resistance readings.

The rate of increase in conductivity at any instant was determined by measuring the slope of the 1/R - Time curve. From these $\Delta 1/R / \Delta t$ values, the rate of solution expressed as the rate of increase of concentration of silver chloride in the subsaturated solution, was calculated by using the relationship that a change of 1×10^{-6} ohms^{-1} in 1/R is equivalent to a change in concentration of silver chloride of (1000 x cell constant) / Λ_{AgCl} g.equivs./l. Substituting the value of Λ_{AgCl} at 25° = 137.97, this factor becomes 0.500×10^{-6} for cell B and 0.565×10^{-6} for cell E. The rates of solution dc/dt were expressed in g.equivs./l./min./volume of suspension used. The initial

TABLE 8

Run	Stirring Rate revs/min	Initial Concentrations $[Ag^+]x10^5$ g.equivs/l	$[Cl^-]x10^5$ g.equivs/l	$[Ag^+][Cl^-]$ x 10^{10}	* % Subsaturation
		Cell B :	3 mls. suspension A		
6	600	1.115	1.115	1.244	30
8	600	1.116	1.115	1.244	30
9	320	1.115	1.115	1.244	30
12	600	1.577	0.789	1.244	30
13	600	0.789	1.577	1.244	30
		Cell B :	5 mls. suspension B		
26	700	1.116	1.116	1.245	30
		Cell B :	5 mls. suspension C		
27	700	1.116	1.116	1.245	30
		Cell E :	2 mls. suspension D		
46	530	1.116	1.115	1.244	30

* Percentage Subsaturation = $\dfrac{\text{Solubility Product} - \text{Initial concentration product}}{\text{Solubility Product}} \times 100$

FIGURE 12

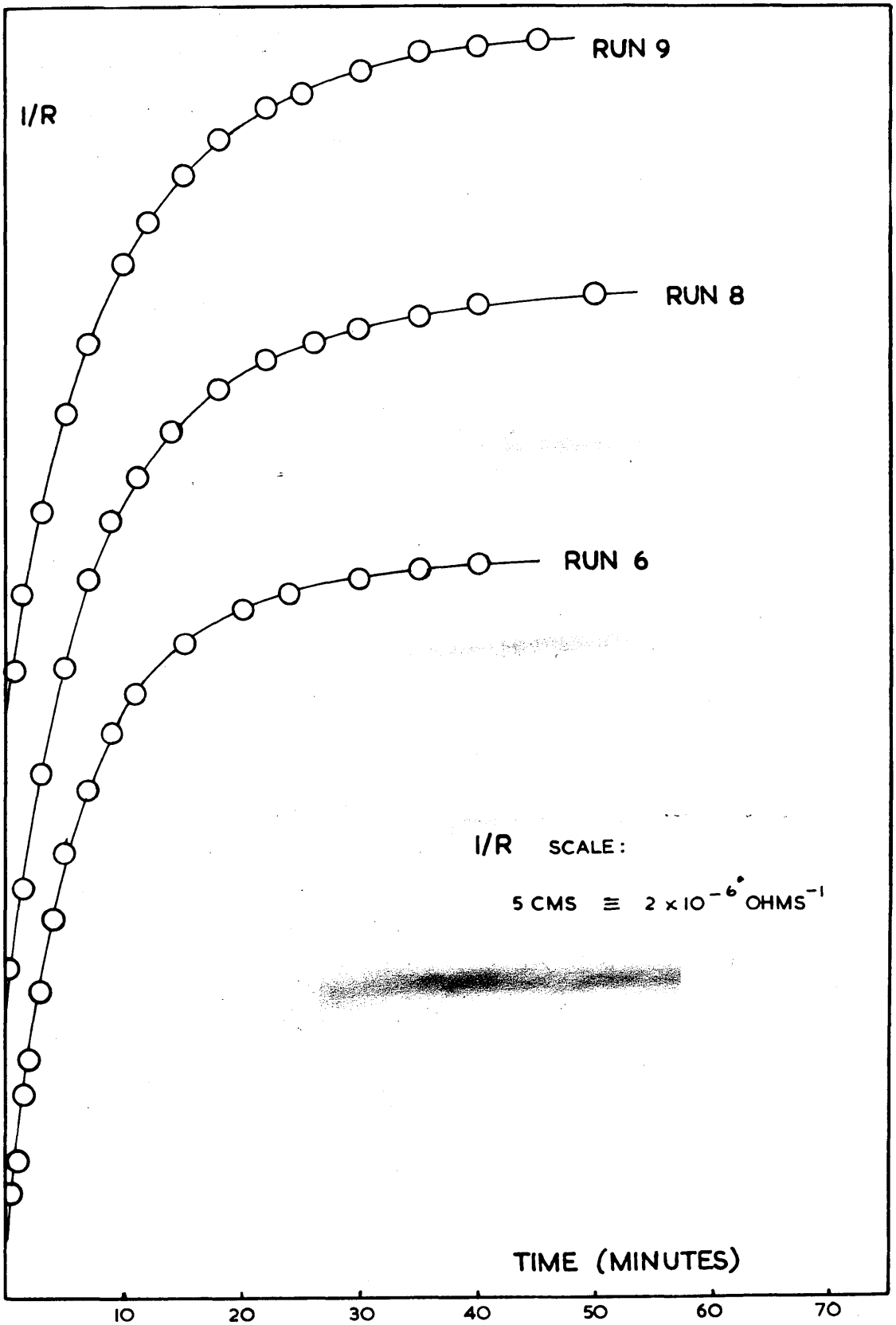

RUN 9
RUN 8
RUN 6
1/R
1/R SCALE:
5 CMS ≡ 2 x 10⁻⁶ OHMS⁻¹
TIME (MINUTES)
10
20
30
40
50
60
70

FIGURE 13

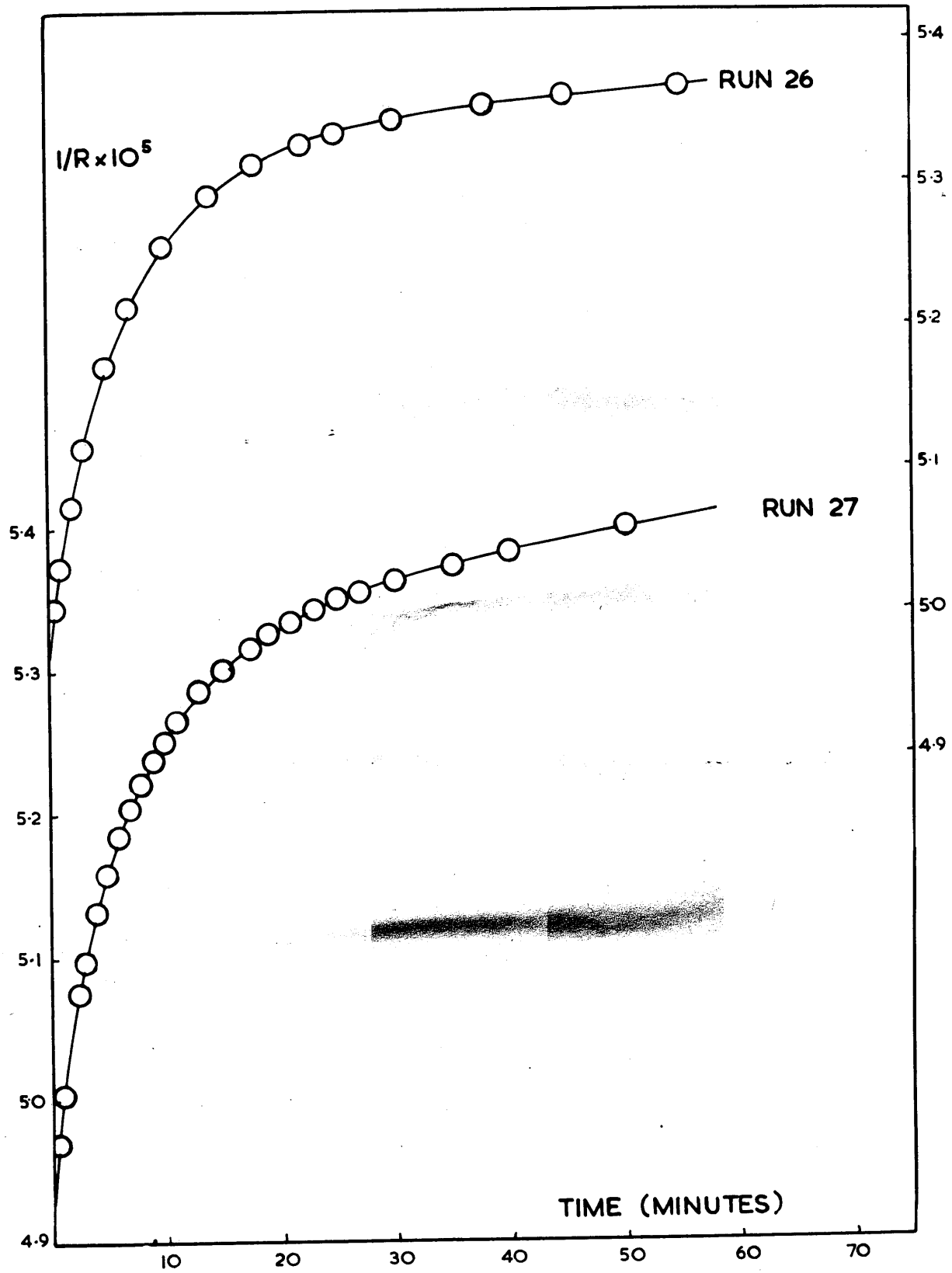
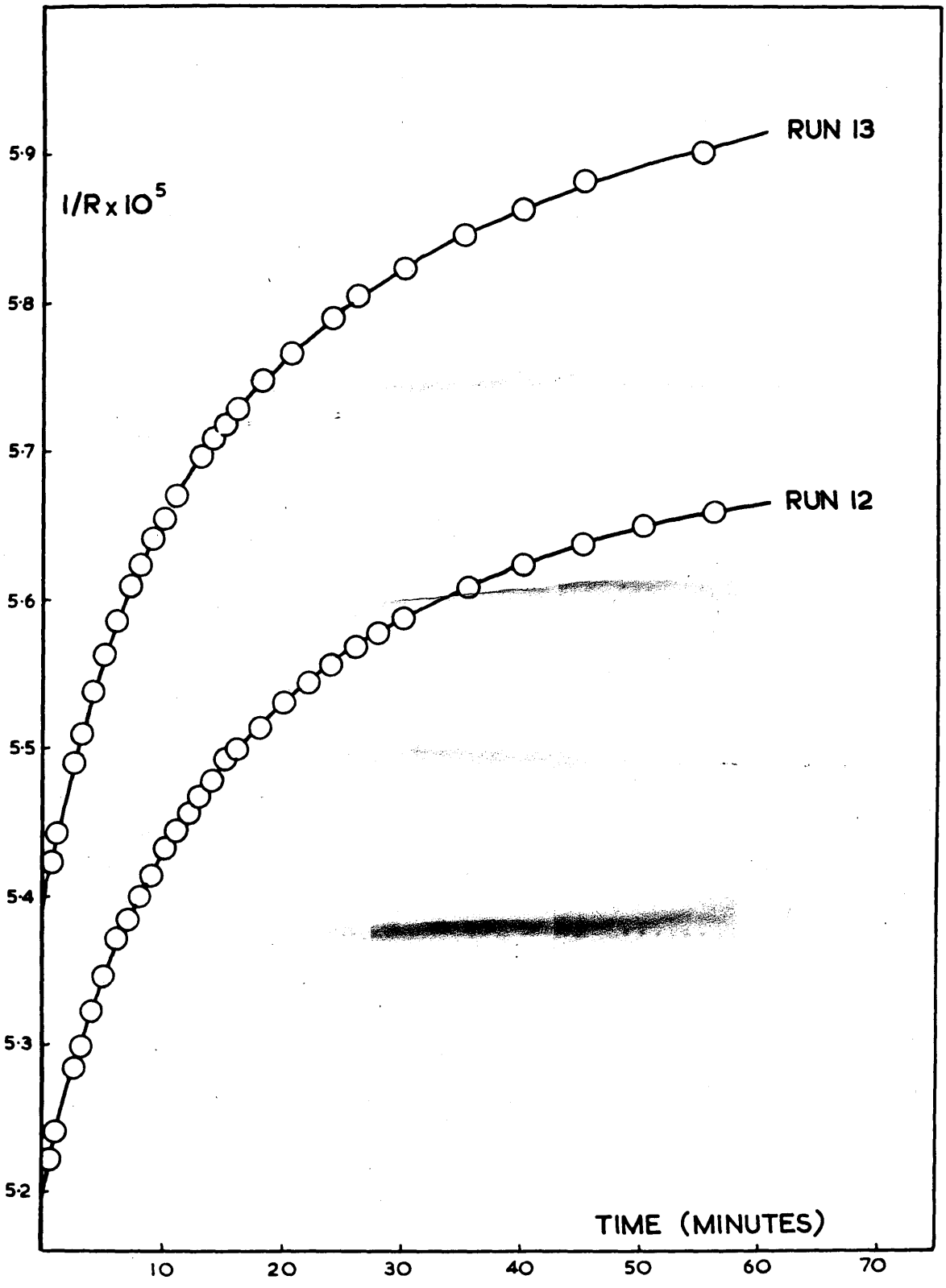

RUN 26
RUN 27
1/R x 10^5
5·4
5·3
5·2
5·1
5·0
4·9
TIME (MINUTES)
10
20
30
40
50
60
70

FIGURE 14


RUN 13
RUN 12
1/R x 10^5
5·9
5·8
5·7
5·6
5·5
5·4
5·3
5·2
TIME (MINUTES)
10
20
30
40
50
60
70

rate of solution was obtained by applying the short extrapolation of the solution curve to zero time.

The difference between the initial and subsequent values of 1/R was used to calculate the amount of silver chloride dissolved at any instant, and since the total amounted to only 4-5 % of the weight of seed present, changes in the surface area due to solution could be neglected.

The results of the experiments summarised in Table 8 in which the concentrations of silver and chloride ions in the subsaturated solutions were equivalent are given in Tables 9 and 10.

When the rate of solution dc/dt was plotted against $(c_o - c)$, where c_o is the solubility of silver chloride and c is the concentration at time t in g.equivs./l., good straight lines passing through the origin were obtained. These are shown in figures 15, 16 and 19 and the slopes are listed in Table 11. The equation

$$dc/dt = K (c_o - c) \quad \ldots\ldots\ldots (1)$$

where K is a constant depending on the surface area of seed crystals, and $(c_o - c)$ is a measure of the subsaturation, can therefore be used to represent the kinetics of dissolution of silver chloride seed crystals into

subsaturated solutions containing equivalent concentrations of silver and chloride ions at 25°C.

Reproducibility : Time plots of 1/R for runs 6 and 8 in which identical conditions were used are shown in figure 12. dc/dt is plotted against $(c_o - c)$ for these experiments in figure 15 and the same value is obtained for the slopes of the lines (Table 11) within experimental error.

Stirring rate : In run 9, the conditions prevailing in runs 6 and 8 were reproduced but the rate of stirring was reduced. The time plot of 1/R is shown in figure 12 and and the results of run 9 are given in Table 9. The slope of the straight line in figure 15 obtained on plotting dc/dt against $(c_o - c)$, is given in Table 11. It is seen that it is less than the mean value obtained from runs 6 and 8 and this will be discussed later.

Seed concentrations : Different seed suspensions were used in runs 26 and 27 while the remaining experimental conditions were identical. Time plots of 1/R are shown in figure 13 and the results of both experiments are given in Table 10. Plots of dc/dt against $(c_o - c)$ are shown in figure 16 : values of the slopes of the lines are given in Table 11 and will be discussed later.

TABLE 9

$\frac{1}{R}.10^5$	Amount AgCl dissolved x 10^5	$[Ag^+]$ x10^5 g.equivs/l	$[Cl^-]$ x10^5 g.equivs/l	$(c_o - c)$ x10^5 g.equivs/l	$\frac{\Delta 1/R}{\Delta t}$ x10^7	$\frac{dc}{dt}$ x10^7
Run 6.						
4.960	0	1.115	1.115	0.222	7.5	3.75
5.060	0.050	1.165	1.165	0.172	5.7	2.85
5.160	0.100	1.215	1.215	0.122	4.4	2.20
5.260	0.150	1.265	1.265	0.072	2.4	1.20
5.360	0.200	1.315	1.315	0.022	0.74	0.37
Run 8.						
5.000	0	1.116	1.115	0.222		
5.100	0.050	1.166	1.165	0.172	5.6	2.80
5.200	0.100	1.216	1.215	0.122	3.9	1.95
5.300	0.150	1.266	1.265	0.072	2.1	1.05
5.400	0.200	1.316	1.315	0.022	0.80	0.40
Run 9.						
4.926	0	1.116	1.115	0.222		
5.026	0.050	1.166	1.165	0.172	4.0	2.00
5.126	0.100	1.216	1.215	0.122	2.8	1.40
5.226	0.150	1.266	1.265	0.072	1.8	0.90
5.326	0.200	1.316	1.315	0.022	0.5	0.25

TABLE 10

$\frac{1}{R} \cdot 10^5$	Amount AgCl dissolved x 10^5	$[Ag^+]$ x10^5 g.equivs/l	$[Cl^-]$ x10^5 g.equivs/l	$(c_o - c)$ x10^5 g.equivs/l	$\frac{\Delta 1/R}{\Delta t}$ x10^7	$\frac{dc}{dt}$ x10^7
Run 26						
4.960	0	1.116	1.116	0.221		
5.060	0.050	1.166	1.166	0.171	4.8	2.4
5.160	0.100	1.216	1.216	0.121	3.0	1.5
5.260	0.150	1.266	1.266	0.071	1.7	0.85
5.360	0.200	1.316	1.316	0.021	0.12	0.06
Run 27						
4.924	0	1.116	1.116	0.221		
5.024	0.050	1.166	1.166	0.171	5.7	2.85
5.124	0.100	1.216	1.216	0.121	3.62	1.81
5.224	0.150	1.266	1.266	0.071	1.90	0.95
5.324	0.200	1.316	1.316	0.021	0.56	0.28
Run 46						
4.224	0	1.1155	1.1155	0.221		
4.274	0.0282	1.1437	1.1437	0.193		
4.324	0.0565	1.1720	1.1720	0.165	4.36	2.46
4.374	0.0847	1.2002	1.2002	0.137	3.14	1.77
4.424	0.1030	1.2185	1.2185	0.118	2.32	1.31
4.474	0.1312	1.2467	1.2467	0.090	1.52	0.86
4.524	0.1695	1.2850	1.2850	0.052	0.82	0.46

TABLE 11

Run	Stirring Rate revs/min	Seed Suspension	Initial Ionic Ratio $[Ag^+]/[Cl^-]$	Slopes of Lines K	K'
Experiments at 25°C					
6	600	A	1/1	0.168 } 0.165	
8	600	A	1/1	0.162 }	
9	320	A	1/1	0.112	
12	600	A	2/1		0.084
13	600	A	1/2		0.104
26	700	B	1/1	0.126	
27	700	C	1/1	0.150	
46	530	D	1/1	0.120	
Experiments at 15°C					
32	720	C	1/1	0.080	
33	720	C	1/1	0.088	
45	530	D	1/1	0.085	
Experiments at 35°C					
29	720	C	1/1	0.141	
31	720	C	1/1	0.138	
43	530	D	1/1	0.154	

FIGURE 15

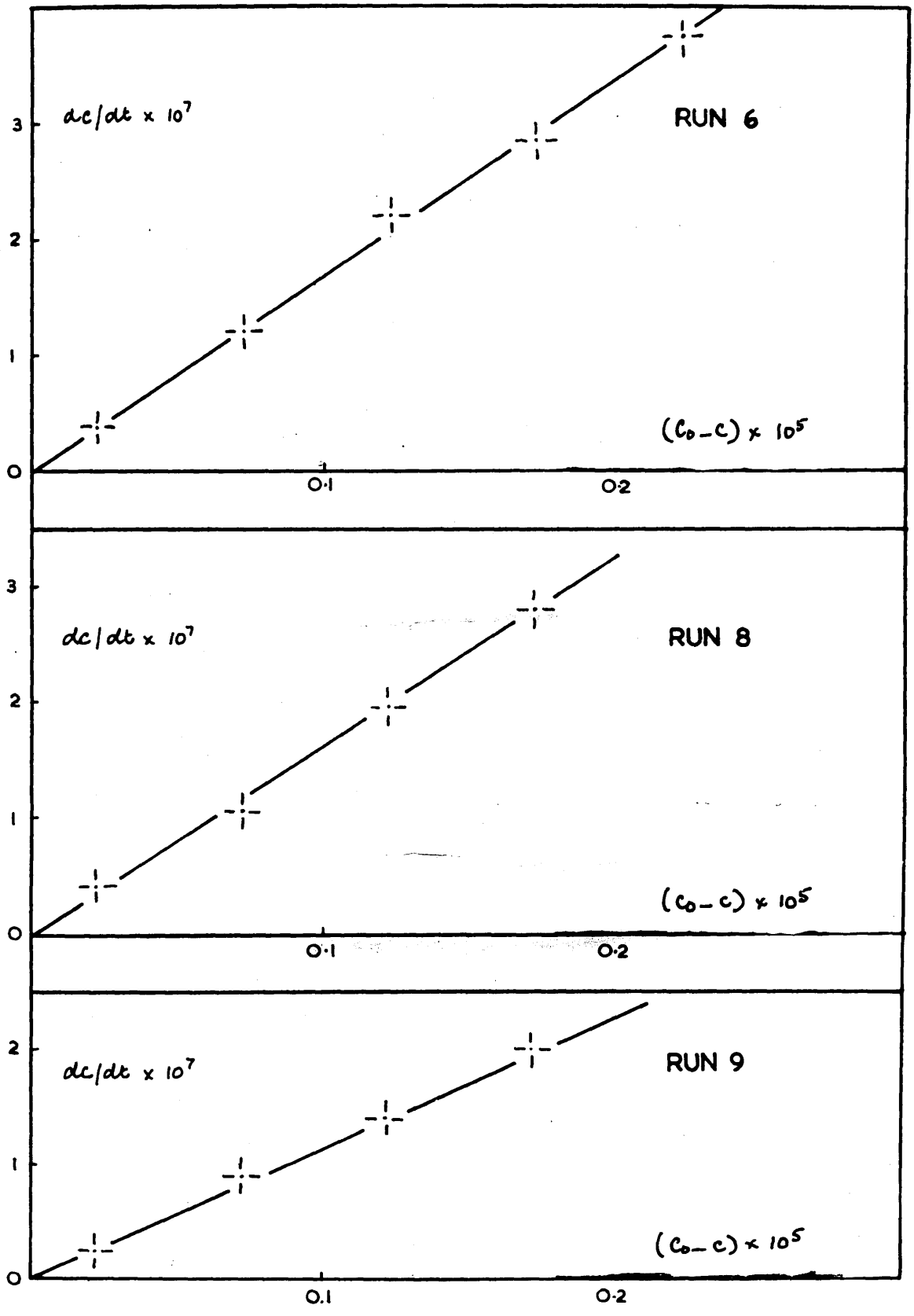
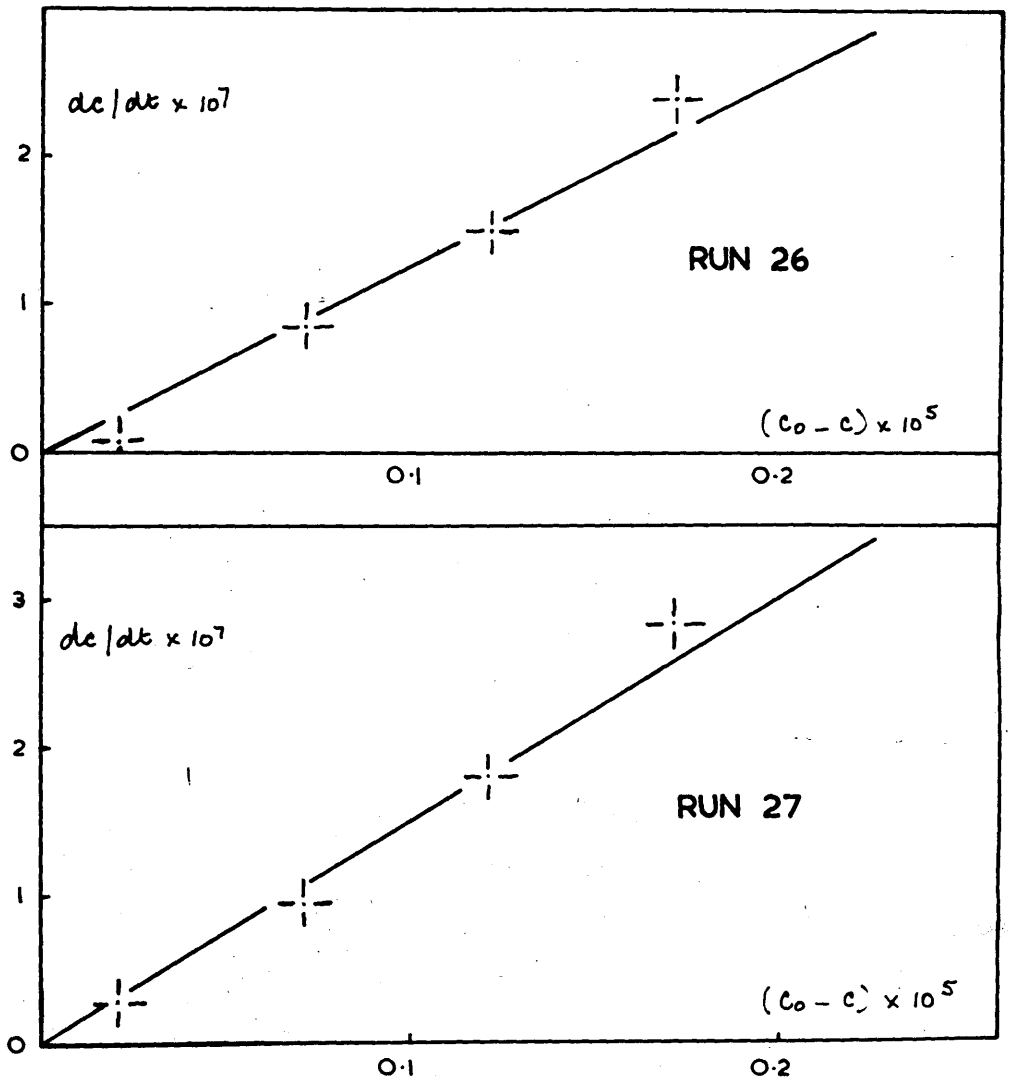

dc/dt x 10^7
RUN 6
(C0 - C) x 10^5
0
1
2
3
0·1
0·2
dc/dt x 10^7
RUN 8
(C0 - C) x 10^5
0
1
2
3
0·1
0·2
dc/dt x 10^7
RUN 9
(C0 - C) x 10^5
0
1
2
0.1
0·2

FIGURE 16


dc/dt x 10^7
2
1
0
RUN 26
(c0 - c) x 10^5
0·1
0·2
dc/dt x 10^7
3
2
1
0
RUN 27
(c0 - c) x 10^5
0·1
0·2

Experiments at non-equivalent concentrations : Runs 12 and 13 in which the initial ionic ratio, $[Ag^+]/[Cl^-]$, was not unity are summarised in Table 8 and the time plots of 1/R are shown in figure 14.

These experiments were interpreted in terms of the amount of silver chloride to be dissolved before equilibrium was reached. If $[Ag^+]_e$ and $[Cl^-]_e$ are the equilibrium concentrations of silver and chloride ions,

$$[Ag^+]_e[Cl^-]_e = \text{solubility product} = c_o^2 \quad \ldots (2)$$

If $[Ag^+]$ and $[Cl^-]$ are the ionic concentrations at any time t,

$$[Ag^+]_e - [Ag^+] = [Cl^-]_e - [Cl^-] \quad \ldots\ldots\ldots (3)$$

Substituting (2) in (3),

$$[Ag^+]_e - [Ag^+] = c_o^2/[Ag^+]_e - [Cl^-]$$

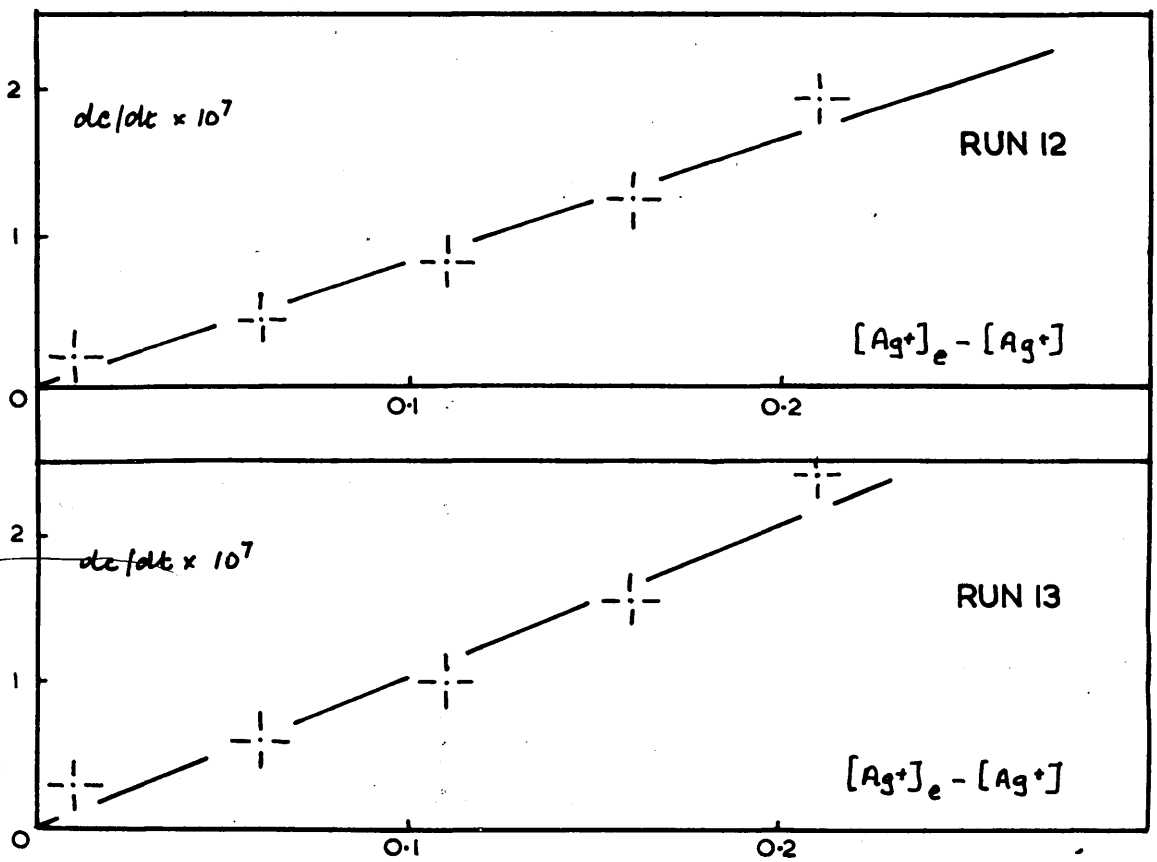
and $$[Ag^+]_e^2 - ([Ag^+] - [Cl^-])[Ag^+]_e - c_o^2 = 0 \quad \ldots (4)$$

$[Ag^+]$, $[Cl^-]$ and c_o^2 were known, $[Ag^+]_e$ was calculated to be 1.788×10^{-5} g.equivs./l. for run 12 and 0.999×10^{-5} g.equivs/l for run 13. Values of $([Ag^+]_e - [Ag^+])$, the amount of silver chloride to be dissolved before equilibrium is reached, are given in Table 12. When dc/dt was plotted

TABLE 12

$\frac{1}{R} \times 10^5$	Amount AgCl dissolved $\times 10^5$	$[Ag^+] \times 10^5$	$[Cl^-] \times 10^5$	$[Ag^+]_e - [Ag^+]_t$	$\frac{\Delta 1/R}{\Delta t} \times 10^7$	$\frac{dc}{dt} \times 10^7$
Run 12						
5.204	0	1.578	0.789	0.210	3.84	1.92
5.304	0.050	1.628	0.839	0.160	2.50	1.25
5.404	0.100	1.678	0.889	0.110	1.66	0.83
5.505	0.150	1.728	0.939	0.060	0.88	0.44
5.605	0.200	1.778	0.989	0.010	0.40	0.20
Run 13						
5.400	0	0.789	1.578	0.210	4.80	2.40
5.500	0.050	0.839	1.628	0.160	3.10	1.55
5.600	0.100	0.889	1.678	0.110	1.98	0.99
5.700	0.150	0.939	1.728	0.060	1.20	0.60
5.800	0.200	0.989	1.778	0.010	0.59	0.29

FIGURE 17


dc/dt x 10^7
RUN 12
[Ag+]e - [Ag+]
2
1
0
0·1
0·2
dc/dt x 10^7
RUN 13
[Ag+]e - [Ag+]
2
1
0
0·1
0·2

against ($[Ag^+]_e$ - $[Ag^+]$) good straight lines passing through the origin were obtained. These are shown in figure 17 and the slopes are given in Table 11. The first order equation

$$dc/dt = K' ([Ag^+]_e - [Ag^+])$$

where K' is a constant depending on the surface area, can therefore be used to represent the kinetics of dissolution of silver chloride into subsaturated solutions containing non-equivalent concentrations of silver and chloride ions.

Experiments at 15° and 35°C.

The concentrations of silver and chloride ions in the subsaturated solutions in these experiments were equivalent, and they are summarised in Table 13. Time plots of 1/R for runs 43 and 45, typical of experiments at 35°C and 15°C respectively, are shown in figure 18.

From the equation

$$\Delta c = \frac{1000 \times \text{cell constant}}{\Lambda_{AgCl}} . \Delta 1/R$$

it was calculated that a change of 1×10^{-6} $ohms^{-1}$ in 1/R was equivalent to a change in concentration of silver chloride of 0.615×10^{-6} g.equivs./l. for cell B and 0.696×10^{-6} g.equivs./l. for cell E at 15°C and 0.417×10^{-6}

TABLE 13

Run	Stirring Rate revs/min	Seed Suspension	Initial Concentrations $[Ag^+] \times 10^5$ g.equiv/l	$[Cl^-] \times 10^5$ g.equiv/l	$[Ag^+][Cl^-] \times 10^{10}$	Cell	% Subsaturation*
Experiments at 15°C							
32	720	C	0.6180	0.6180	0.3819	B	46
33	720	C	0.6180	0.6180	0.3819	B	46
45	530	D	0.6200	0.6200	0.3844	E	46
Experiments at 35°C							
29	720	C	1.800	1.800	3.240	B	22
31	720	C	1.813	1.814	3.289	B	21
43	530	D	1.800	1.800	3.240	E	22

5 mls. suspension C used in each experiment

2 mls. suspension D used in each experiment

$$\text{* \% Subsaturation} = \frac{\text{Solubility Product - Initial concentration product}}{\text{Solubility Product}} \times 100$$

TABLE 14

$\frac{1}{R}.10^5$	Amount AgCl dissolved x 10^5	$[Ag^+]$ x 10^5 g.equivs/l	$[Cl^-]$ x 10^5 g.equivs/l	$(c_o - c)$ x 10^5 g.equivs/l	$\frac{\Delta 1/R}{\Delta t}$ x10^7	$\frac{dc}{dt}$ x10^7
Run 32						
2.2075	0	0.6180	0.6180	0.222		
2.2575	0.0308	0.6488	0.6488	0.191	2.60	1.60
2.3075	0.0615	0.6795	0.6795	0.160	2.10	1.29
2.3575	0.0923	0.7103	0.7103	0.130	1.62	1.00
2.4075	0.1230	0.7410	0.7410	0.099	1.22	0.75
2.4575	0.1538	0.7718	0.7718	0.068	0.66	0.41
Run 33						
2.190	0	0.6180	0.6180	0.222		
2.240	0.0308	0.6488	0.6488	0.191	3.04	1.87
2.290	0.0615	0.6795	0.6795	0.160	2.55	1.57
2.340	0.0923	0.7103	0.7103	0.130	2.08	1.28
2.390	0.1230	0.7410	0.7410	0.099	1.34	0.82
2.440	0.1538	0.7718	0.7718	0.068	0.77	0.47
2.490	0.1846	0.8026	0.8026	0.037	0.22	0.14
Run 45						
2.010	0	0.6200	0.6200	0.220		
2.060	0.0348	0.6548	0.6548	0.185	2.66	1.85
2.110	0.0696	0.6896	0.6896	0.150	1.80	1.25
2.160	0.1044	0.7244	0.7244	0.116	1.40	0.97
2.210	0.1392	0.7592	0.7592	0.081	0.97	0.68
2.260	0.1740	0.7940	0.7940	0.046	0.23	0.16

TABLE 15

$\frac{1}{R}.10^5$	Amount AgCl dissolved $\times 10^5$ g.equivs/l	$[Ag^+] \times 10^5$ g.equivs/l	$[Cl^-] \times 10^5$ g.equivs/l	$(c_o - c) \times 10^5$ g.equivs/l	$\frac{\Delta 1/R}{\Delta t} \times 10^7$	$\frac{dc}{dt} \times 10^7$
Run 29						
8.985	0	1.800	1.800	0.236		
9.085	0.0417	1.842	1.842	0.194	6.62	2.76
9.185	0.0834	1.883	1.883	0.153	4.84	2.02
9.285	0.1251	1.925	1.925	0.111	3.54	1.48
9.385	0.1668	1.967	1.967	0.069	2.50	1.04
9.485	0.2085	2.009	2.009	0.027	1.30	0.54
Run 31						
8.950	0	1.8130	1.8140	0.222		
9.050	0.0417	1.8547	1.8557	0.181	5.80	2.42
9.150	0.0834	1.8964	1.8974	0.140	4.80	2.00
9.250	0.1251	1.9381	1.9381	0.097	3.24	1.35
9.350	0.1668	1.9798	1.9808	0.056	1.74	0.72
9.450	0.2085	2.0215	2.0225	0.014	0.64	0.27
Run 43						
8.010	0	1.800	1.800	0.236		
8.110	0.0472	1.847	1.847	0.189	6.92	3.27
8.160	0.0708	1.871	1.871	0.165	5.72	2.70
8.210	0.0944	1.894	1.894	0.142	4.62	2.18
8.260	0.118	1.918	1.918	0.118	3.94	1.86
8.310	0.1416	1.942	1.942	0.094	3.00	1.42
8.360	0.1652	1.965	1.965	0.071	2.10	0.99
8.410	0.1888	1.989	1.989	0.047	0.96	0.45

FIGURE 18

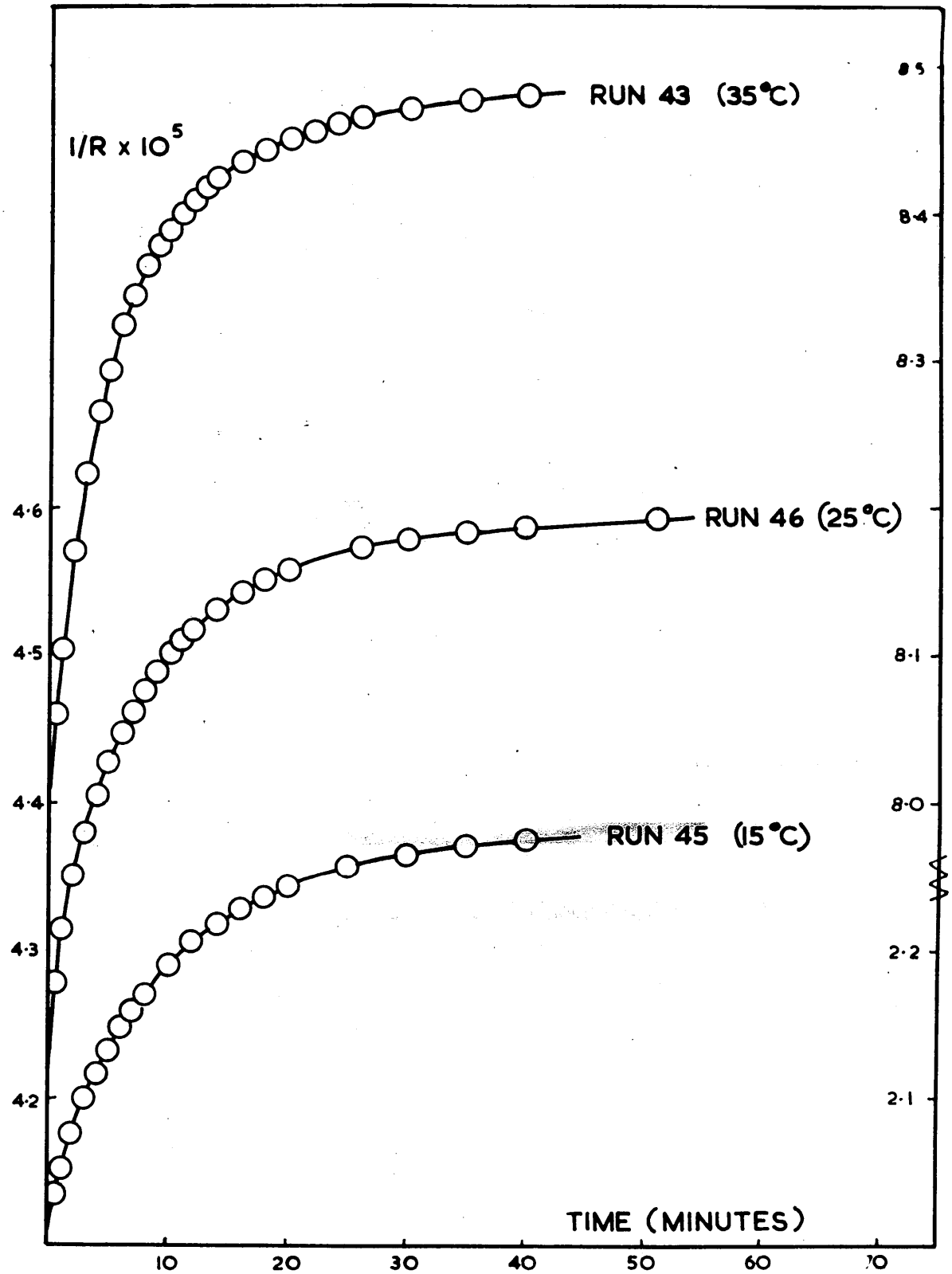

1/R x 10^5
RUN 43 (35°C)
RUN 46 (25°C)
RUN 45 (15°C)
TIME (MINUTES)
4·6
4·5
4·4
4·3
4·2
8·5
8·4
8·3
8·1
8·0
2·2
2·1
10
20
30
40
50
60

FIGURE 19

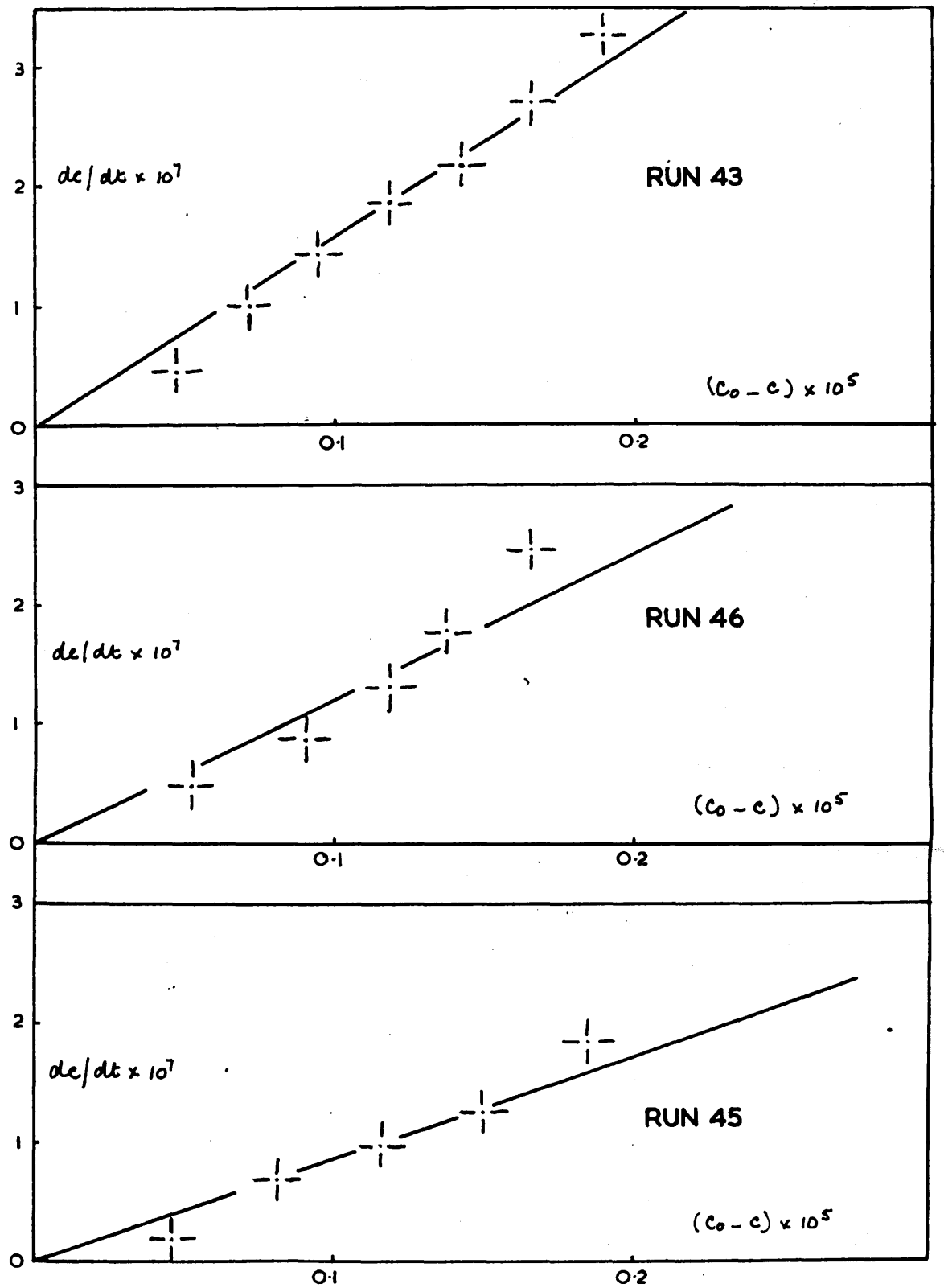
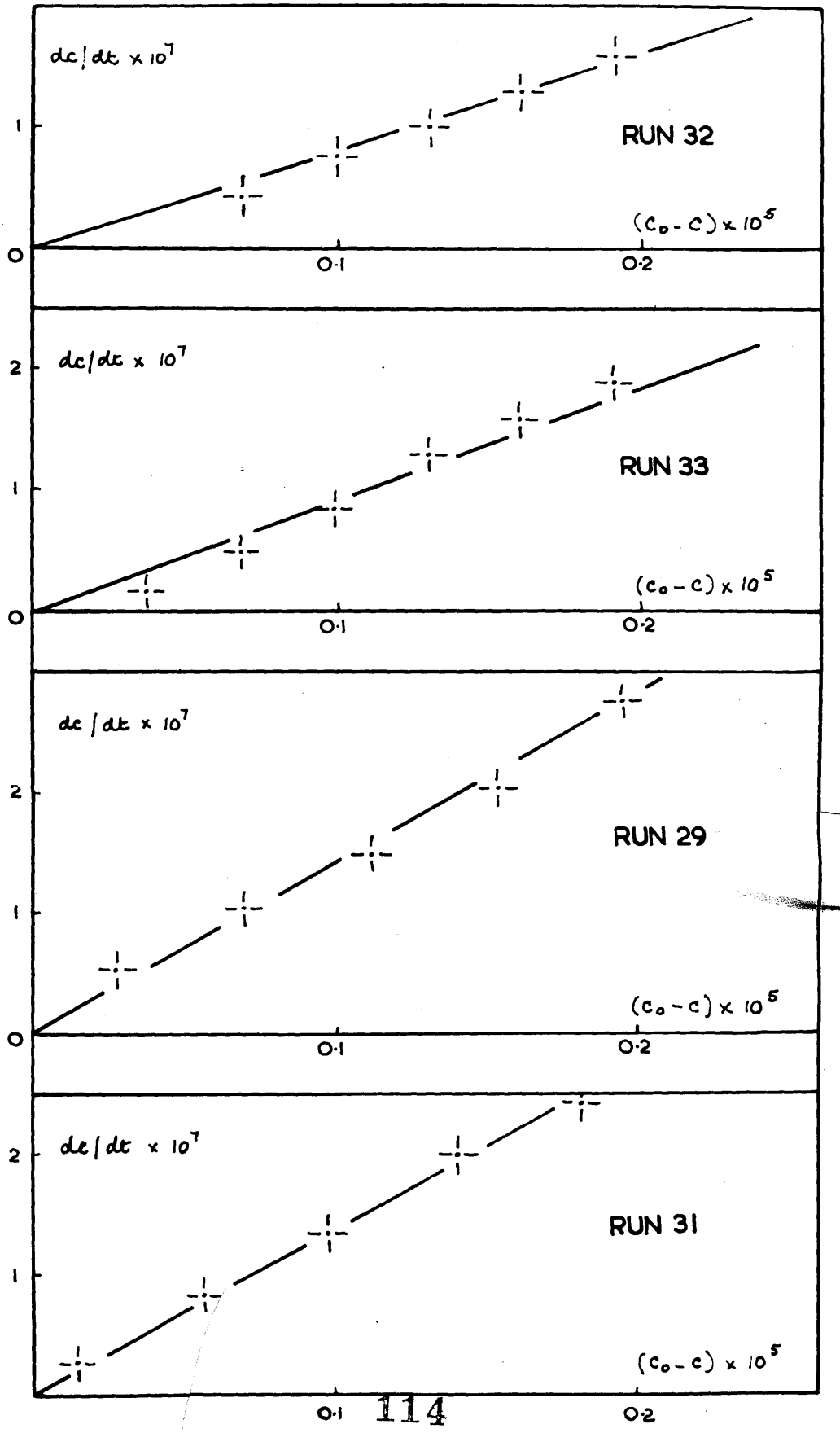

3
2
1
0
dc/dt x 10^7
RUN 43
(C0 - C) x 10^5
0·1
0·2
3
2
1
0
dc/dt x 10^7
RUN 46
(C0 - C) x 10^5
0·1
0·2
3
2
1
0
dc/dt x 10^7
RUN 45
(C0 - C) x 10^5
0·1
0·2

FIGURE 20


dc/dt x 10^7
RUN 32
(c_o - c) x 10^5
0·1
0·2
0
1
dc/dt x 10^7
RUN 33
(c_o - c) x 10^5
0·1
0·2
0
1
2
dc/dt x 10^7
RUN 29
(c_o - c) x 10^5
0·1
0·2
0
1
2
dc/dt x 10^7
RUN 31
(c_o - c) x 10^5
0·1
0·2
1
2

g.equivs./l. for cell B and 0.472 $x10^{-6}$ g.equivs./l. for cell E at 35°C. The rates of solution were derived as described for the 25°C experiments.

The results of experiments summarised in Table 13 are given in Tables 14 and 15.

When dc/dt was plotted against $(c_o - c)$ for each experiment, good straight lines passing through the origin were again obtained. These are shown in figures 19 and 20 and the slopes are given in Table 11.

The equation $dc/dt = K (c_o - c)$ ..... (1)

used to represent the kinetics of dissolution of silver chloride seed crystals into subsaturated solutions containing equivalent concentrations of silver and chloride at 25°C was therefore also applicable at 15°C and 35°C. These results indicated that the dissolution under these experimental conditions was of the first order with respect to the degree of supersaturation at each temperature.

2. Dissolution of Silver Chromate.

The dissolution of silver chromate seed crystals into subsaturated solutions has been studied at 25°C. The solubility of silver chromate (0.88×10^{-4} moles/l)

determined in Part 1 of the present work was used.

When studying the crystal growth of silver chromate, pH runs exactly analogous to those done in the conductivity cell were carried out. This procedure was repeated in the dissolution experiments so that any change in pH during dissolution could be detected. As in the crystallisation work the pH of the cell solution remained constant to within ± 0.01 pH units for at least 30 minutes after the addition of seed suspension. The pH was determined at the end of each dissolution run so that corrections could be made for hydrolysis.

The silver chromate dissolution experiments are summarised in Table 16 and the typical smooth curve obtained on plotting 1/R against time for run 2 is shown in figure 21.

From the pH of the cell solution at the end of each dissolution experiment, the value of

$$\alpha = [HCrO_4^-]/[CrO_4^=] = \{H^+\}f_2/f_1k_a \quad ,$$

was obtained using the method outlined in Part 1, pages 31-33. The change in the ionic concentrations of silver and chromate ions, $\Delta[Ag^+]$ and $\Delta[CrO_4^=]$ during dissolution were calculated from the observed specific conductivity as described in Part 1, pages 56-57.

The initial value of 1/R was obtained by extrapolating the dissolution curve to zero time. The difference between it and subsequent values of 1/R was used to calculate the amount of silver chromate dissolved at any instant. The corresponding rates of solution dm/dt were obtained by measuring the slopes of the 1/R - time curves at these points and correcting for $\Delta[HCrO_4^-]$.

Detailed analyses of the experiments of Table 16 are given in Table 17. When the rate of dissolution of silver chromate, dm/dt, is plotted against $(\sqrt[3]{K_s} - \sqrt[3]{I.P.})$, where I.P. is the ionic product $[Ag^+]^2[CrO_4^=]$ at time t, and K_s is the solubility product of silver chromate, good straight lines passing through the origin were obtained and are shown in figure 22. The expression

$$dm/dt = K_1 (\sqrt[3]{K_s} - \sqrt[3]{I.P.})$$

can therefore be used to represent the kinetics of dissolution of silver chromate seed crystals into subsaturated solution, where K_1 is a constant dependent on the surface area of seed crystals. This dissolution, like that of silver chloride under similar experimental conditions, therefore obeys a first order rate equation.

TABLE 16

Run	pH	Stirring Rate revs/min	Initial Concentrations $[Ag^+]x10^4$ moles/l.	$[CrO_4^=]x10^4$ moles/l.	$[Ag^+]^2[CrO_4^=]$ x 10^{12}	Cell	% Subsaturation*
1	7.6	600	1.60	0.74	1.89	B	31
2	7.2	600	1.66	0.69	1.91	B	30
3	6.9	500	1.71	0.61	1.78	B	35

Seeds prepared by fast precipitation

$$\text{* \% Subsaturation} = \frac{\text{Solubility Product} - \text{Initial concentration product}}{\text{Solubility Product}} \times 100$$

TABLE 17

$\frac{1}{R}$ x10^4	$[Ag^+]$ x10^4 moles/l.	$[CrO_4^=]$ x10^4 moles/l.	I.P. x10^{12}	$(\sqrt[3]{I.P.})$ x10^4	$(\sqrt[3]{K_s} - \sqrt[3]{I.P.})$ x10^4 moles/l.	$\frac{\Delta 1/R}{\Delta t}$ x10^6	$\frac{dm}{dt}$ x10^7
Run 1 : $\alpha = 0.08$; $\Delta[Ag^+] = 0.0490 \times 10^{-4}$; $\Delta[CrO_4^=] = 0.0236 \times 10^{-4}$							
6.80	1.600	0.740	1.89	1.24	0.160		
6.90	1.649	0.763	2.08	1.28	0.121	3.02	6.95
7.00	1.698	0.786	2.27	1.31	0.083	1.85	4.37
7.10	1.747	0.810	2.47	1.35	0.045	0.92	2.17
7.20	1.796	0.833	2.69	1.39	0.006	0.31	0.73
Run 2 : $\alpha = 0.20$; $\Delta[Ag^+] = 0.0495 \times 10^{-4}$; $\Delta[CrO_4^=] = 0.0225 \times 10^{-4}$							
7.04	1.660	0.692	1.91	1.24	0.157		
7.14	1.710	0.714	2.09	1.28	0.120	4.66	10.5
7.24	1.759	0.737	2.28	1.32	0.081	2.94	6.62
7.34	1.809	0.759	2.48	1.35	0.043	1.25	2.81
7.44	1.858	0.782	2.70	1.39	0.004	0.31	0.70
Run 3 : $\alpha = 0.41$; $\Delta[Ag^+] = 0.0504 \times 10^{-4}$; $\Delta[CrO_4^=] = 0.0209 \times 10^{-4}$							
5.875	1.714	0.608	1.79	1.213	0.184		
5.975	1.764	0.629	1.96	1.251	0.146	4.17	8.71
6.075	1.815	0.650	2.14	1.288	0.109	2.74	5.73
6.175	1.865	0.671	2.33	1.326	0.071	1.82	3.80
6.275	1.916	0.691	2.54	1.402	0.033	0.95	1.99

FIGURE 21

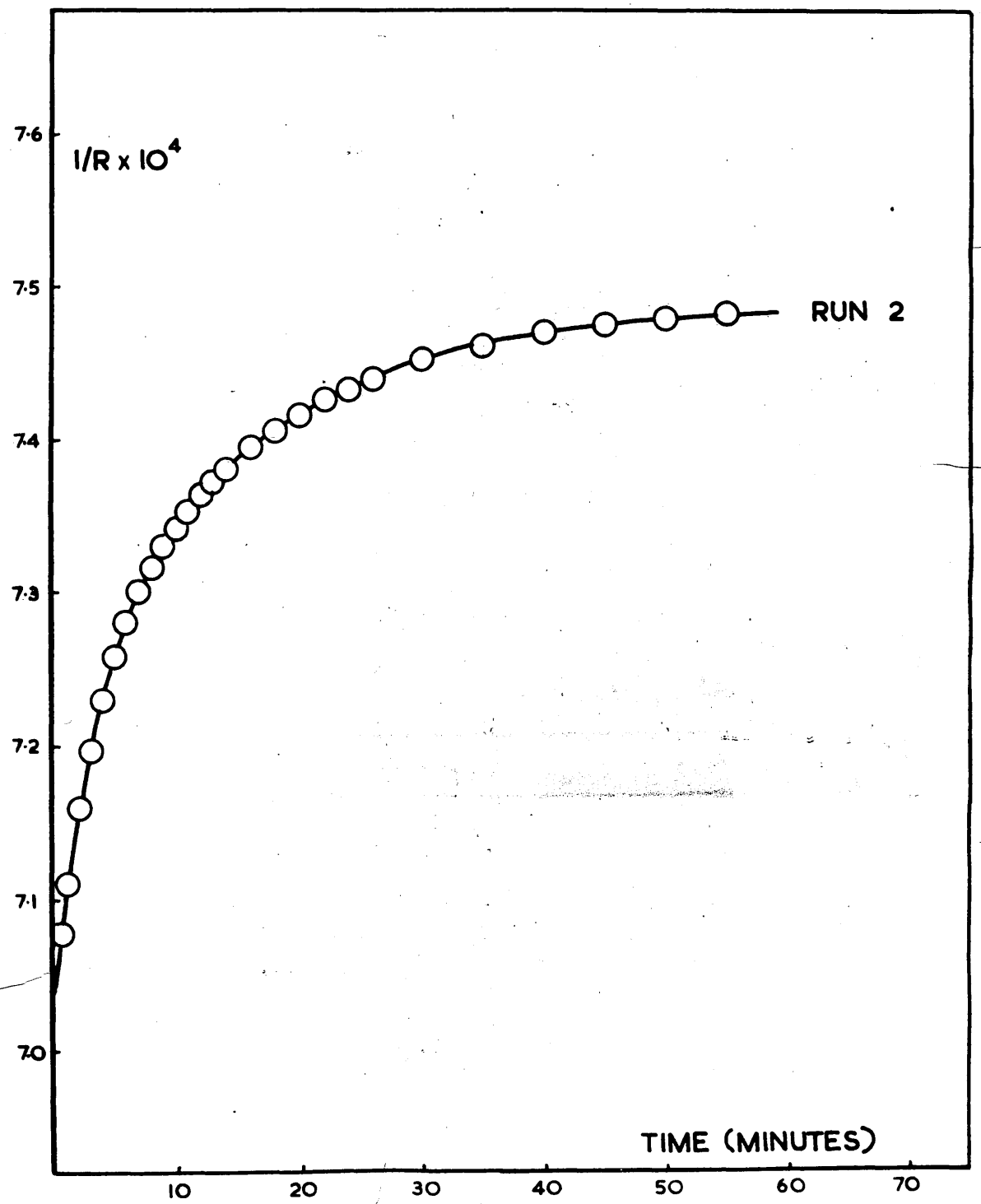
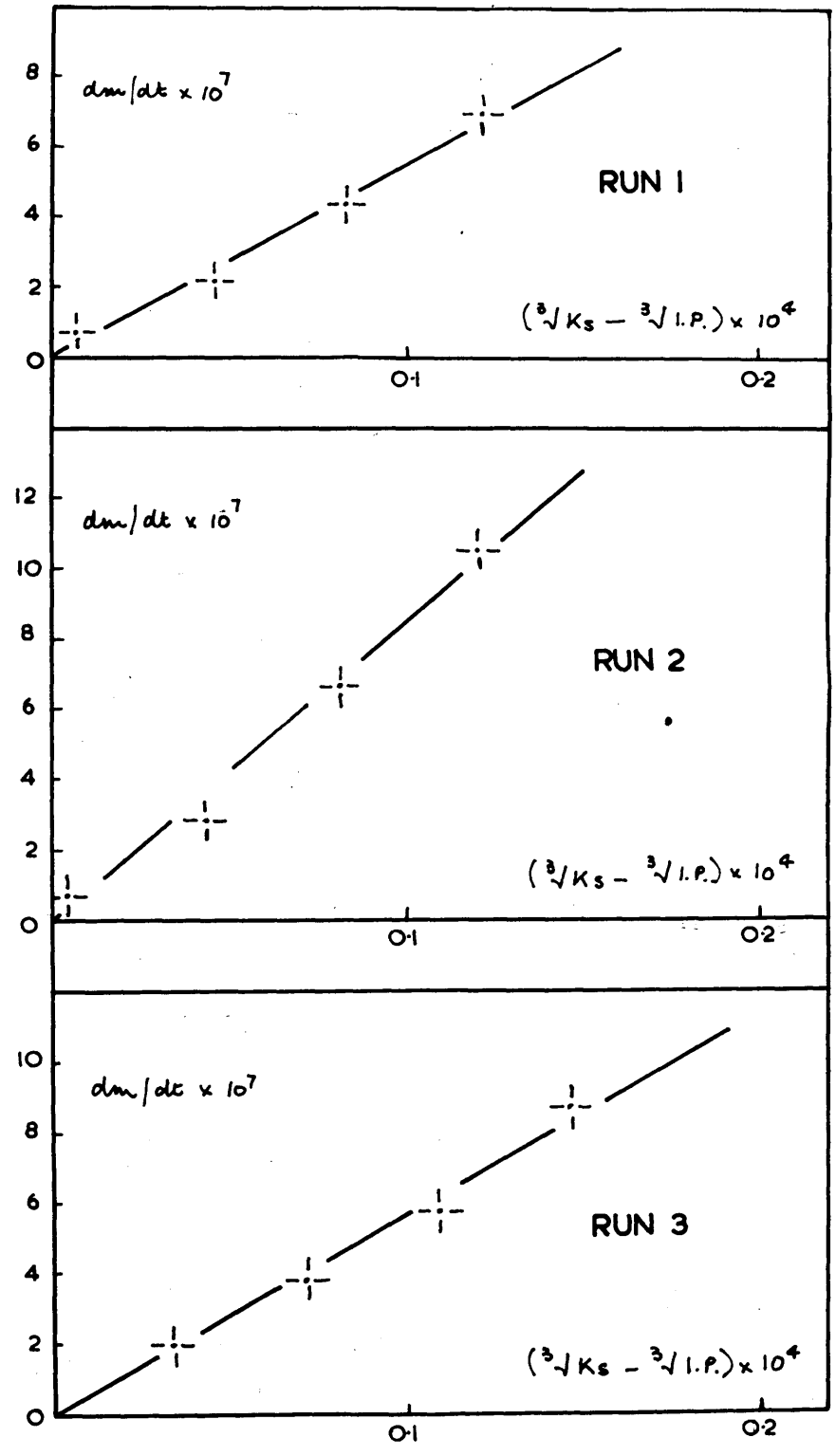


FIGURE 22


dm/dt x 10^7
RUN 1
(∛Ks − ∛I.P.) x 10^4
0·1
0·2
dm/dt x 10^7
RUN 2
(∛Ks − ∛I.P.) x 10^4
dm/dt x 10^7
RUN 3
(∛Ks − ∛I.P.) x 10^4

DISCUSSION

Although several heterogeneous reactions such as crystallisation have been shown to follow higher order rate equations, first order kinetics have been obtained for the majority of dissolution reactions studied. Most workers agree, therefore, that dissolution is a diffusion controlled process . Nernst's original theory is criticised, however, because he suggested that all heterogeneous reactions were diffusion controlled and that the thickness of the diffusion layer was constant.

In the present work the dissolution of silver chloride seed crystals into subsaturated solutions containing equivalent concentrations of silver and chloride ions, at 15°, 25° and 35°C, was found to obey the first order rate equation

$$dc/dt = K''s\,(c_o - c)$$
$$= K\,(c_o - c) \qquad \ldots\ldots\ldots (1)$$

where K" is the rate constant, c is the concentration of solute at time t , c_o is the solubility and s is the surface area of the solute. The dependence of the rate

constant K (equation 1) on the surface area of the solute is seen by comparing the values of K (Table 11) for runs 26 and 27 in which different seed suspensions were used.

K = 0.126 for run 26 when wt. of seeds added was 3.25mgs

K = 0.150 " " " " " " " " 4.55mgs.

Assuming that the seed crystals were uniform cubes,

$$s \propto (w/d)^{2/3}$$

where s is the surface area of w g. of crystals and d is the density of silver chloride. The K value for run 26, K_{26}, was derived from that for run 27 as follows:

$$K_{26} = 0.150 \times (3.25/4.55)^{2/3} = 0.120 .$$

The good agreement between the calculated and experimental values indicated that the average size of the seed crystals in different stock suspensions was similar.

In the equation relating the stirring rate of diffusion controlled dissolution reactions to the rate constant K

$$K \propto (\text{revs/min.})^{a},$$

values of a between 0.56 and 1.0 have been suggested. In the present work, when the rate of stirring was reduced

from 600 revs./min. (runs 6 and 8) to 320 revs./min.(run 9), the mean value of K for runs 6 and 8 was reduced from 0.165 to 0.112 - see Table 11. This corresponded to an a value of about 0.61.

The temperature coefficient for the dissolution of silver chloride was obtained from the rate constants of runs 45, 46 and 43 at 15°, 25° and 35°, respectively. These experiments were all done at the same stirring rate, using suspension D. The concentration of the sample of seed suspension used at 35°C was slightly greater than that at 15° and 25°C and the K value of run 43 was corrected as outlined above so that all corresponded to the same surface area; values are given in Table 18. The activation energy E was derived graphically from the equation

$$\ln K = \ln A - (E/RT) \quad ,$$

where A is a constant; R is the gas constant and K is the rate constant at the absolute temperature T. Values of log K at 15°, 25° and 35°C are given in Table 18, and log K is plotted against 1/T in figure 23. E, calculated from the slope of the straight line, was ~5.0 k.cals. per mole which may be compared with the activation energy for diffusion reactions, ranging from 2.8 to 6.5 k.cals. per mole depending on the solute and solvent.[84]

In a diffusion-controlled reaction,

$$K = Ds / \delta$$

where K is the rate constant, D is the diffusion coefficient and s is the surface area of the solute; δ is the thickness of the diffusion layer. Assuming that δ is constant at different temperatures and if s is also constant as in runs 45, 46, 43,

$$K = \text{constant} \times D \qquad \text{and} \qquad D \propto 1/\eta$$

$$\therefore \log K = \log \text{constant} - \log \eta$$

where η is the viscosity of the solution. Values of $\log \eta$ at 15°, 25° and 35°C are given in Table 18. It is seen from figure 24 that log K approximately follows $\log \eta$.

All the above evidence points to diffusion as the rate determining step in the dissolution of silver chloride seed crystals into subsaturated solutions containing equivalent concentrations of silver and chloride, and this might be interpreted in terms of the rapid formation at the surface of a layer of hydrated ions of concentration corresponding to saturation. The rate of dissolution is then controlled by the rate at which ions diffuse from this layer to the bulk of the solution.

Using this picture in the experiments in which the initial ionic ratio, $[Ag^+]/[Cl^-]$ is not unity, the surface layer will contain unequal concentrations of silver and chloride ions. If $[Ag^+] > [Cl^-]$ in the subsaturated solution, the silver ion will be in excess and a potential difference ψ will be set up between the surface layer and the solution. The concentrations of silver and chloride ions in the surface layer may be written

$$c_o \exp(-\psi/kT) \quad \text{and} \quad c_o \exp(\psi/kT)$$

respectively, where c_o is the solubility of silver chloride and k is Boltzmann's constant. If the concentrations of silver and chloride ions in the bulk of the solution are $[Ag^+]$ and $[Cl^-]$, the rate of diffusion of silver ions from the surface is

$$K''s \left\{ c_o \exp(-\psi/kT) - [Ag^+] \right\},$$

and this must be equal to the corresponding term for chloride ions

$$K''s \left\{ c_o \exp(\psi/kT) - [Cl^-] \right\},$$

i.e. $$c_o \exp(-\psi/kT) - [Ag^+] = c_o \exp(\psi/kT) - [Cl^-] \quad ..(5)$$

or $$c_o \exp(2\psi/kT) + ([Ag^+] - [Cl^-]) \exp(\psi/kT) - c_o = 0 \quad .....(6)$$

Comparing this with equation (4),

$$[Ag^+]_e^2 + ([Ag^+] - [Cl^-]) [Ag^+]_e - c_o^2 = 0 \quad \ldots\ldots\ldots (4)$$

$[Ag^+]_e = c_o \exp(\psi/kT)$, and $[Cl^-]_e = c_o \exp(- \psi /kT)$.

These may be considered as equivalent to the surface concentrations of these ions.

It is interesting that first order kinetics were also obtained for the dissolution of silver chromate indicating that with this unsymmetrical electrolyte also, diffusion plays an important part. Complications arise here, however, due to corrections for hydrolysis.

TABLE 18

Run	45	46	43
Temperature (^{o}C)	15	25	35
Temperature (^{o}A)	288	298	308
$1/T \times 10^{3}$	3.47	3.36	3.25
K	0.085	0.120	0.154
log K	- 1.07	- 0.921	- 0.813
$\eta \times 10^{3}$	11.45	8.95	7.21
log η	- 1.94	- 2.05	- 2.14

FIGURE 23

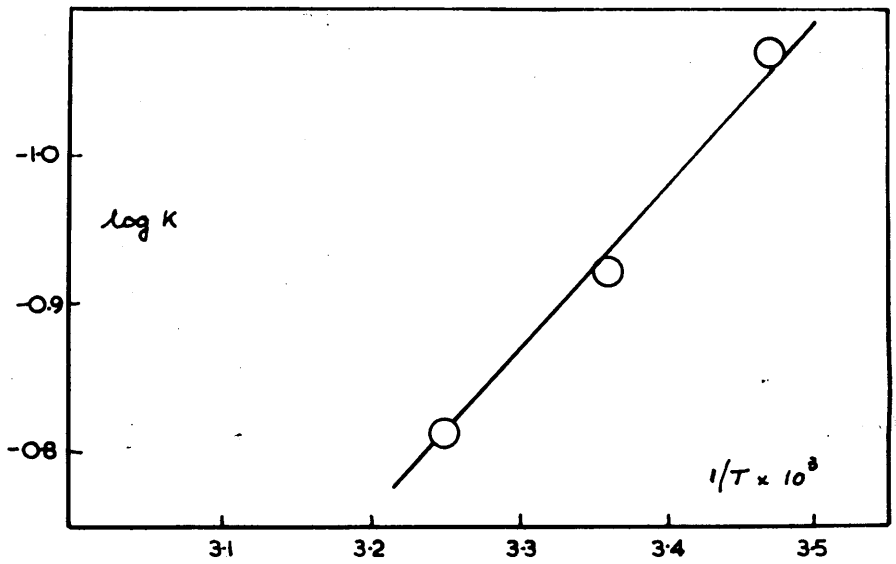
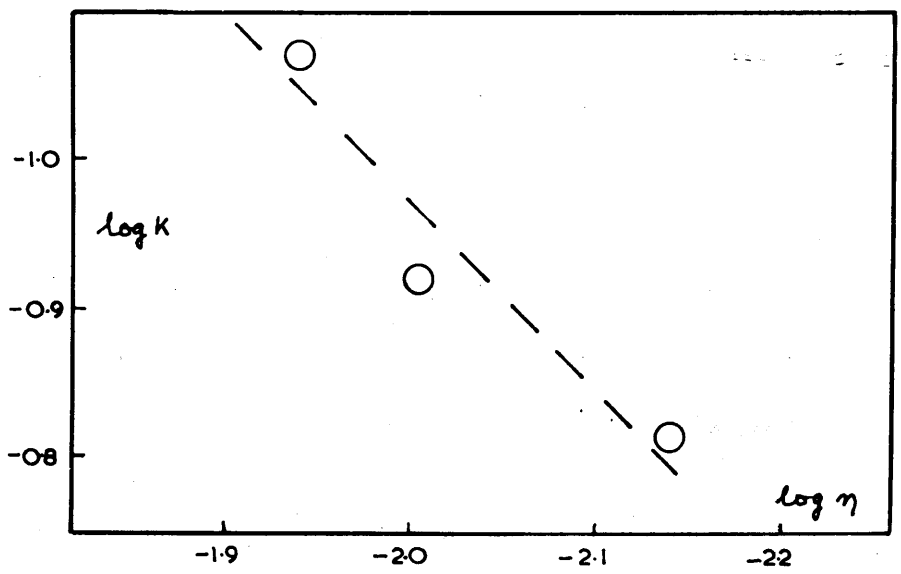


FIGURE 24



PART 3

CRYSTAL GROWTH OF SILVER CHLORIDE

AT VARYING IONIC STRENGTH

AND

IN THE PRESENCE OF SURFACE ACTIVE AGENTS.

INTRODUCTION

A simple derivation of the relationship between the activity coefficients of the reactants and the rate constants of bimolecular reactions has been devised by Bjerrum[85]. He assumed that in the reaction,

$$A + B \rightleftharpoons M^* \rightarrow X + Y,$$

the reactants A and B were in equilibrium with the activated complex M* so that

$$K = \{M^*\}/\{A\}\{B\} , \quad \ldots\ldots\ldots (1)$$

where braces indicate the activities of reactants, and the rate of reaction was proportional to the concentration of the activated complex.

$$\text{i.e. Rate of reaction} = k^* [M^*] , \quad \ldots\ldots (2)$$

square brackets representing molar concentrations. On replacing the activities in equation (1) by the products of the concentrations and activity coefficients,

$$[M^*] = K[A][B] . \frac{f_A . f_B}{f_{M^*}}$$

and therefore from equation (2),

$$\text{Rate of reaction} = k^*K\,[A][B].\,\frac{f_A.f_B}{f_{M^*}} \quad \ldots\ldots (3)$$

The rate of reaction could also be written in terms of k, the observed specific rate constant,

$$\text{Rate of reaction} = k\,[A][B]\,. \quad \ldots\ldots (4)$$

By combining equations (3) and (4),

$$k = k^*K.\,\frac{f_A.f_B}{f_{M^*}} = k_o\,\frac{f_A.f_B}{f_{M^*}}$$

$$\text{or} \quad \log k = \log k_o + \log f_A.f_B/f_{M^*}\,, \quad \ldots\ldots (5)$$

where $k_o = k^*K$.

This relationship between rate constants and activity coefficients has also been established by statistical treatment of the problem in terms of the charge and size of the activated complex[86]: this leads to essentially the same result as the simple Bjerrum derivation given above.

If the reactants and products were all non-electrolytes, the factor $f_A.f_B/f_{M^*}$ would be almost independent of the concentration and so the observed velocity constant k would also remain virtually constant. When ions are involved, however, the value of k may be constant in a

particular solution, but it will vary with the total ionic concentration, whether due to the reactants themselves or to added electrolytes.

The effect of electrolytes has been divided into two categories : the primary and secondary salt effects. The former refers to the influence of the electrolyte concentration on the activity coefficients f_A, f_B and f_{M*}, whereas the latter is concerned with actual changes in the concentration of the reacting ions resulting from the addition of electrolytes.

In the present work supersaturated solutions of silver chloride of varying ionic strength have been prepared by the addition of potassium nitrate. The rate of growth of silver chloride seed crystals from these solutions has been followed conductimetrically at 25°C.

The variation in activity coefficient with concentration in dilute aqueous solutions at 25°C may be represented by the simple limiting form of the Debye-Huckel equation,

$$- \log f = 0.51 z^2 \sqrt{I} \quad ,$$

where I is the ionic strength and z is the valency of the ion. It follows, therefore, that

$$\log f_A . f_B / f_{M*} = 0.51 \sqrt{I} (z_A^2 + z_B^2 + z_{M*}^2) \quad ..... \quad (6)$$

Since the activated complex is made up of A and B, its charge will be the algebraic sum of those of A and B,

$$\text{i.e.} \quad z_{M*} = z_A + z_B \ ,$$

and, from equation (6),

$$\log f_A.f_B/f_{M*} = 0.51\sqrt{I}\,(2z_Az_B)$$
$$= 1.02\, z_Az_B\sqrt{I} \qquad \ldots\ldots\ldots (7)$$

Substituting (7) in (5),

$$\log k = \log k_o + 1.02\, z_Az_B\sqrt{I} \ . \qquad \ldots\ldots\ldots (8)$$

If the crystallisation of silver chloride followed this equation we should get ($z_A = 1$ and $z_B = -1$)

$$\log k = \log k_o - 1.02\sqrt{I}.$$

The range of ionic strengths which could conveniently be used to study the variation in k in the present work was limited by the conductimetric method employed.

Davies and Nancollas[27] have studied the rate of growth of silver chloride seed crystals from supersaturated solutions in the presence of solutions of the surface active agents, potassium eosin, potassium benzoate, potassium naphthalene-2-sulphonate and cetyl trimethylammonium nitrate. They found that eosin greatly retarded growth if present at

concentrations about 10^{-7} moles/l. and completely arrested growth at concentrations greater than about 3×10^{-6} moles/l. The other adsorbates retarded growth at concentrations between 0.5×10^{-5} and 2.0×10^{-5} moles/l. and at higher concentrations, $2\text{-}5 \times 10^{-5}$ moles/l., the growth rate appeared to approach a limiting value. The equation

$$-dc/dt = k (c - c_o)^2 \quad ,$$

previously established[17] for the crystallisation of silver chloride in the absence of adsorbate solutions, was found to be obeyed except in the experiments with eosin. There was, therefore, a sharp contrast between the behaviour of eosin and the other substances studied.

In the present work the crystal growth of silver chloride in the presence of sodium octadecyl sulphate and sodium benzene sulphonate has been followed conductimetrically.

EXPERIMENTAL

The conductivity cell F of modified design was prepared for the work at higher concentrations. The electrode separation was greater than in cells A, B and E so that the cell constant was increased. Interference between the stirrer and the electrodes, which becomes more noticeable as the concentration is increased, was reduced by increasing the diameter of the base of cell F and running the stirrer at the maximum distance from the electrodes. Fine lines were etched on the ground glass joints of the cap and these were aligned before each experiment to fix the position of the electrodes. The error was further reduced by marking the stirrer pulley so that bridge readings were taken with the stirrer in the same position relative to the electrodes.

The cell constant was 0.08990 ± 0.02 %.

Preparation of seed suspensions.

The seed suspensions used in the work on ionic strength and adsorbate effects were prepared in the same way as those used in the silver chloride dissolution experiments. The seed concentrations were measured as

previously described and the values obtained were

Seed Suspension	F	G	H
Concentration (mg./ml.)	1.44	0.46	2.79

Purification of surface active agents.

Sodium octadecyl sulphate : This reagent was kindly supplied 99.8 % pure by I.C.I. Ltd., and was used without further purification.

Sodium benzene sulphonate : This salt was recrystallised from conductivity water.

Experimental procedure.

About 300 g. (see below) of conductivity water were weighed in cell F, which was then equilibrated in a rapid stream of carbon dioxide - free air in the oil thermostat as described on page 19 . The stirring rate was maintained at about 500-600 revs./min. throughout each experiment.

When the resistance of the water had reached a steady value, 10 mls. of a dilute silver nitrate solution were added, followed 1-2 hours later by the required volume (5, 10 or 20 mls.) of potassium nitrate or adsorbate solution. After a further interval of approximately one hour, 10 mls. of a dilute potassium chloride solution were added dropwise

over a period of 6-10 minutes. This slow addition of potassium chloride ensured the stability of the supersaturated solutions formed. The volume of water placed in the cell was such that the final weight of the cell solution was kept constant at 300 g. in all experiments. The concentrations of the dilute silver nitrate and potassium chloride solutions were such that the cell solutions were between 35 % and 45 % supersaturated.

After about two hours the supersaturated solution came to carbon dioxide and temperature equilibrium. The required silver chloride seed suspension was vigorously shaken in a stream of nitrogen for at least 30 minutes before a homogeneous sample was added to the cell and bridge readings were taken as described for the dissolution experiments (page 89).

RESULTS

The crystal growth of silver chloride seed crystals from supersaturated solutions of ionic strength between 0.32×10^{-4} and 10.3×10^{-4} moles/l. has been followed at 25°C. The influence of surface active agents on the rate of growth of silver chloride has also been studied at 25°C.

Solubility and Mobility Values.

The solubility product of silver chloride at zero ionic strength found by Davies and Jones[17] was 1.765×10^{-10} moles^{2}litres^{-2}. The mean activity coefficient of silver chloride, $f_{\pm}$, was obtained from the Davies equation[50]

$$- \log f_{\pm} = 0.5 \, z_{Ag^+} \cdot z_{Cl^-} \left\{ \sqrt{I} / (1 + \sqrt{I}) - 0.2 \, I \right\},$$

where I is the ionic strength, and the solubility of silver chloride, c_o, at each ionic strength, was calculated using the relationship

$$c_o^2 f_{\pm}^2 = 1.765 \times 10^{-10} .$$

The values of c_o for both ionic strength and adsorbate

experiments are given in Tables 20, 21 and 23.

The amount of silver chloride precipitated at any moment was calculated from the equation

$$\Delta c = (1000 / \Lambda) \Delta \kappa$$

which relates Δc the decrease in equivalent concentration of the supersaturated solution to $\Delta \kappa$ the corresponding decrease in the specific conductivity. Λ is the sum of the ionic conductances of silver and chloride ions, calculated from the Onsager equation at 25°C [49],

$$\Lambda = \Lambda_o + (0.2277 \Lambda_o + 59.86) \sqrt{c} \quad .$$

The initial equivalent concentration of silver chloride, c, was kept constant for each experiment and changes in ionic strength due to precipitation in the course of experiments were negligible. The value of Λ_{AgCl}, calculated using the mobility values

$$\Lambda^{\circ}_{Ag} = 61.92 \text{ [48]} \quad \text{and} \quad \Lambda^{\circ}_{Cl} = 76.34 \text{ [48]} \quad \text{at } 25^{\circ}C$$

and a mean c value of 3×10^{-5} g.equivs./l., was $\Lambda_{AgCl} = 137.76$. It was assumed that the mobility values remained constant in supersaturated solutions whose ionic strength was varied by the addition of indifferent electrolyte.

These are summarised in Table 19 and the curves obtained on plotting the reciprocal of the resistance against the time are shown in figures 25 and 26. It is seen from these plots that as the concentration of added potassium nitrate is increased, the degree of scatter in the recorded resistance readings tends to increase and the rate of crystal growth is progressively diminished. The decreased amount of crystallisation and relatively low resistances at high ionic strengths have made it difficult to measure the slope of the 1/R - Time curves accurately.

The second order equation previously established[17] for the growth of silver chloride seed crystals

$$- dc/dt = ks\ (c - c_o)^2, \quad \ldots\ldots\ (1)$$

gives on integration

$$\frac{1}{c - c_o} - \frac{1}{c_i - c_o} = kst \quad , \quad \ldots\ldots\ (2)$$

where c_i is the initial concentration of silver chloride and c is the concentration at time t ; s is the surface area of seed crystals and k is a constant. In the present work an overall rate constant K at constant s

TABLE 19

Run	Initial concentrations $[Ag^+]\times10^5$ g.equivs/l	$[Cl^-]\times10^5$ g.equivs/l	$[Ag^+][Cl^-]$ $\times10^{10}$	$[KNO_3]$ $\times 10^4$ g.equivs/l	Sol. Prod. $\times10^{10}$	* % Super-saturn.
		Cell F : 3 mls. suspension F.				
6	1.6100	1.6100	2.592	-	1.788	45
10	1.6098	1.6100	2.592	-	1.788	45
7	1.6098	1.6100	2.592	1.002	1.812	43
12	1.6100	1.6100	2.592	4.992	1.861	39
11	1.6099	1.6100	2.592	7.419	1.882	38
		Cell F : 3mls. suspension H.				
25	1.6098	1.6100	2.592	-	1.788	45
27	1.6100	1.6100	2.592	-	1.788	45
29	1.6100	1.6100	2.592	5.036	1.862	39
28	1.6100	1.6100	2.592	10.009	1.897	37

* Percentage Supersaturation =

$$\frac{\text{Initial concentration product - solubility product}}{\text{solubility product}} \times 100$$

FIGURE 25

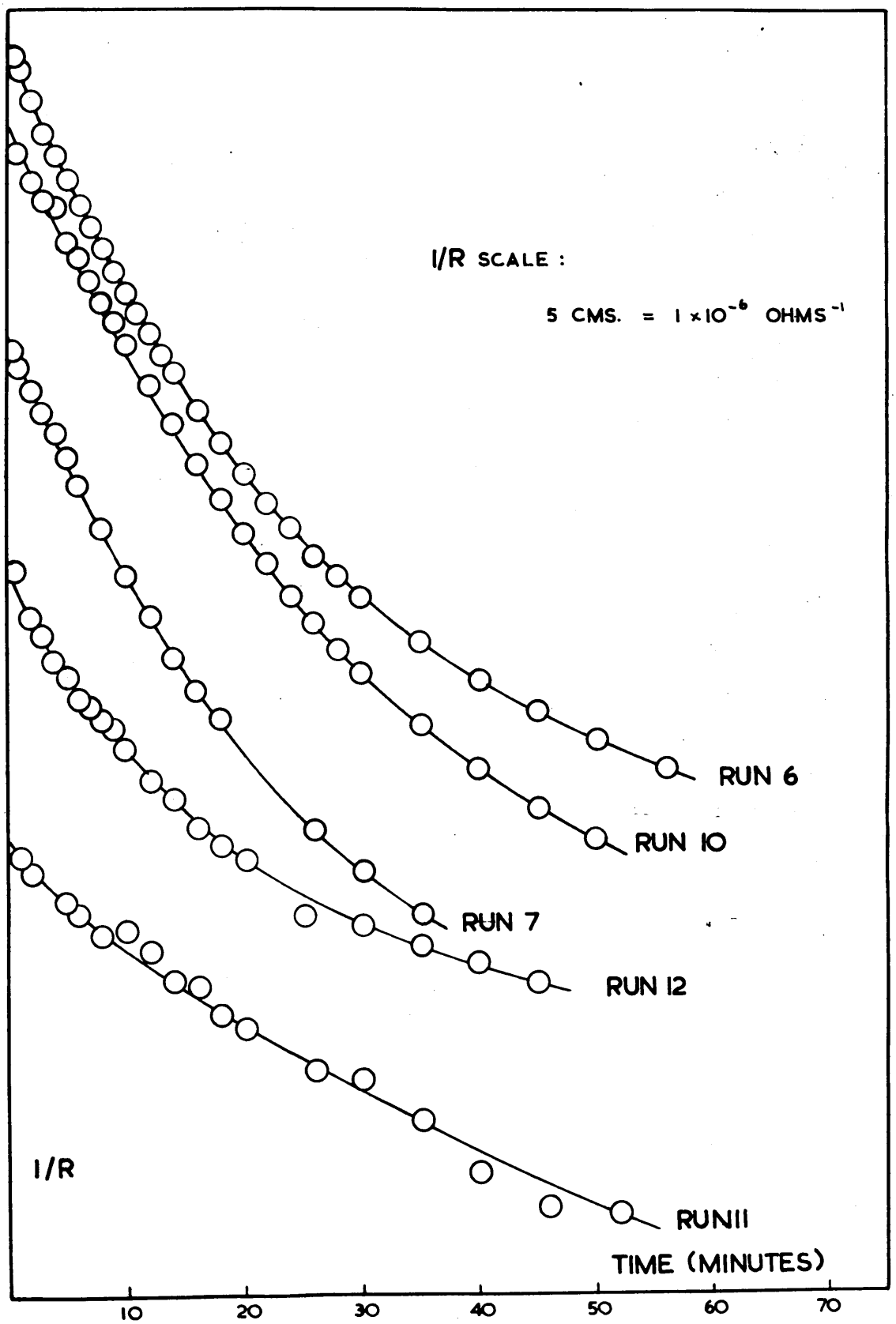
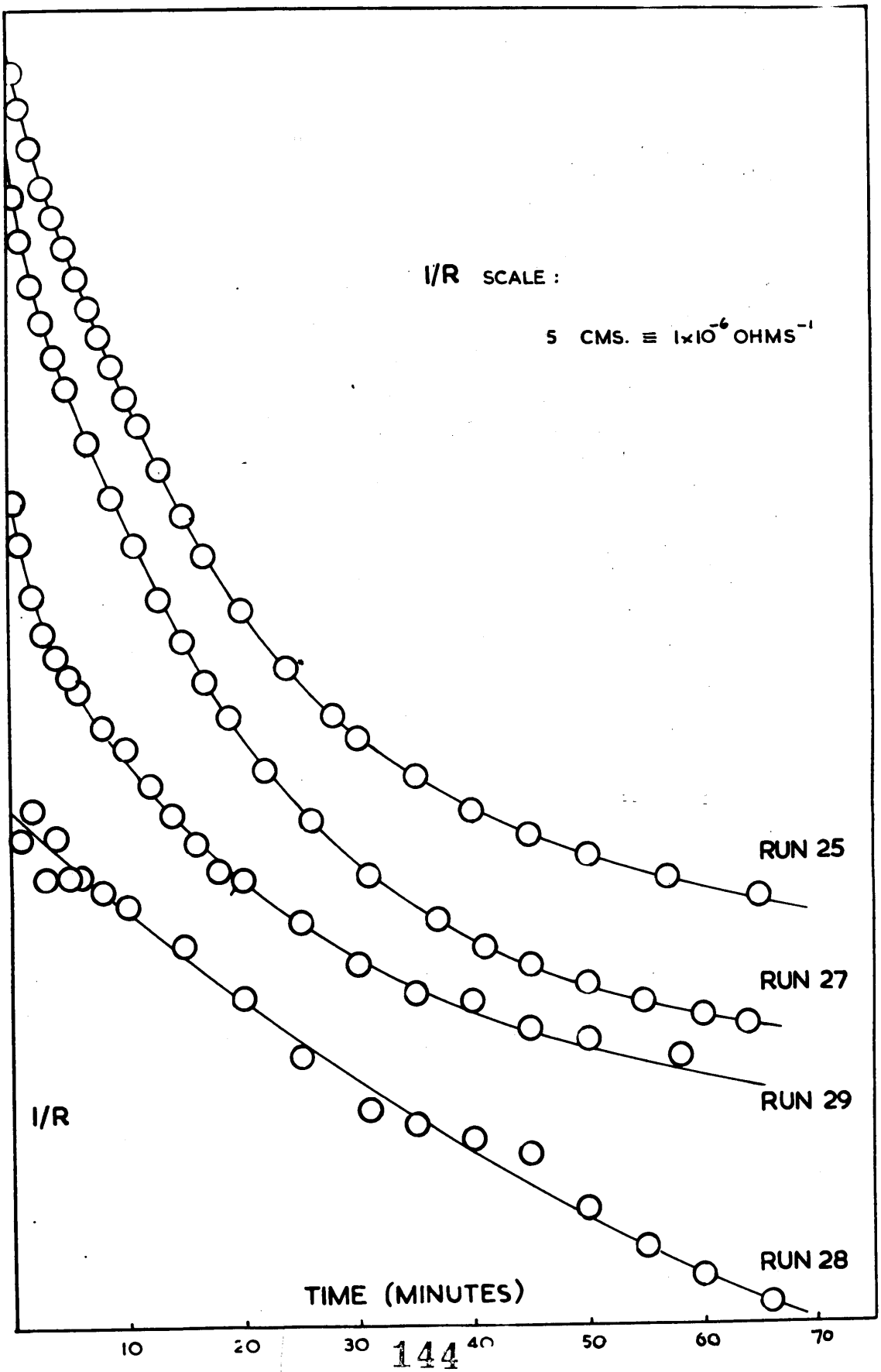

I/R SCALE :
5 CMS. = 1 × 10⁻⁶ OHMS⁻¹
RUN 6
RUN 10
RUN 7
RUN 12
RUN 11
I/R
TIME (MINUTES)
10
20
30
40
50
60
70

FIGURE 26


I/R SCALE :
5 CMS. ≡ 1×10⁻⁶ OHMS⁻¹
RUN 25
RUN 27
RUN 29
RUN 28
I/R
TIME (MINUTES)
10
20
30
40
50
60
70

has been used to replace ks .

The factor (1000 x cell constant) / Λ_{AgCl} relating the change in resistance reading to the change in equivalent concentration of silver chloride, was found to be 0.652 for cell F at 25°C and the rate of crystallisation was expressed in g.equivs./l./min./volume of seed suspension used.

The initial value of 1/R was obtained by applying the short extrapolation of the growth curve to zero time. The difference between the initial and subsequent values of 1/R was used to calculate the quantity of silver chloride precipitated at various times during crystallisation. The total only amounted to 2-4 % of the weight of seed present so that changes in the surface area due to precipitation were neglected.

Detailed results of the experiments summarized in Table 19 are given in Tables 20 and 21.

When the left hand side of equation (2) was plotted against time, straight lines passing through the origin were obtained. These are shown in figures 27 and 28 and the slopes, i.e. rate constants K , are listed in Table 24.

The second order rate equation (1) or (2) can therefore be used to represent the crystal growth of silver chloride seed crystals from supersaturated solutions of varying ionic strength.

TABLE 20

$\frac{1}{R}\cdot 10^4$	Amount AgCl preciptd. $\times 10^5$ g.equiv/l	$[Ag^+]$ $\times 10^5$ g.equiv/l	$[Cl^-]$ $\times 10^5$ g.equiv/l	$c-c_o$ $\times 10^5$	$\frac{1}{c-c_o}$ $\times 10^{-5}$	$1/c-c_o - 1/c_i-c_o$ $\times 10^{-5}$	Time (min)
Run 6:		$c_o = 1.337 \times 10^{-5}$.					
0.520	0	1.6100	1.6100	0.273	3.663		
0.515	0.0326	1.5774	1.5774	0.240	4.167	0.504	5.3
0.510	0.0652	1.5448	1.5448	0.208	4.808	1.145	11.8
0.505	0.0978	1.5122	1.5122	0.175	5.714	2.051	20.1
0.500	0.1304	1.4796	1.4796	0.143	6.993	3.330	32.7
Run 10:		$c_o = 1.337 \times 10^{-5}$.					
0.532	0	1.6098	1.6100	0.273	3.663		
0.527	0.0326	1.5772	1.5774	0.240	4.167	0.504	6.4
0.522	0.0652	1.5446	1.5448	0.208	4.808	1.145	13.6
0.517	0.0978	1.5120	1.5122	0.175	5.714	2.051	21.9
0.512	0.1304	1.4794	1.4796	0.143	6.993	3.330	33.4
Run 7:		$c_o = 1.346 \times 10^{-5}$.					
2.1046	0	1.6098	1.6100	0.264	3.788		
2.0996	0.0326	1.5772	1.5774	0.231	4.329	0.541	6.1
2.0946	0.0652	1.5446	1.5448	0.199	5.025	1.237	13.0
2.0896	0.0978	1.5120	1.5122	0.166	6.024	2.236	21.8
2.0846	0.1304	1.4794	1.4796	0.134	7.463	3.675	37.0
Run 12:		$c_o = 1.364 \times 10^{-5}$.					
8.3724	0	1.6100	1.6100	0.246	4.065		
8.3674	0.0326	1.5774	1.5774	0.213	4.695	0.630	6.5
8.3649	0.0489	1.5611	1.5611	0.197	5.076	1.011	11.8
8.3624	0.0652	1.5448	1.5448	0.181	5.525	1.460	18.3
8.3599	0.0815	1.5285	1.5285	0.165	6.061	1.996	28.7
8.3574	0.0978	1.5122	1.5122	0.148	6.757	2.692	48.6
Run 11:		$c_o = 1.372 \times 10^{-5}$.					
12.1626	0	1.6099	1.6100	0.238	4.202		
12.1601	0.0326	1.5773	1.5774	0.205	4.878	0.676	6.0
12.1576	0.0489	1.5610	1.5611	0.189	5.291	1.089	14.5
12.1551	0.0652	1.5447	1.5448	0.173	5.780	1.578	25.2
12.1526	0.0815	1.5286	1.5285	0.157	6.369	2.167	36.7

TABLE 21

$\frac{1}{R}-.10^4$	Amount AgCl preciptd. $\times10^5$ g.equiv/l	$[Ag^+]$ $\times10^5$ g.equiv/l	$[Cl^-]$ $\times10^5$ g.equiv/l	$c-c_o$ $\times10^5$	$\frac{1}{c-c_o}$ $\times10^{-5}$	$1/(c-c_o) - 1/(c_i-c_o)$ $\times10^{-5}$	Time (min)
Run 25:		$c_o = 1.337 \times 10^{-5}$.					
0.5142	0	1.6098	1.6100	0.273	3.663		
0.5092	0.0326	1.5772	1.5774	0.240	4.167	0.504	2.7
0.5042	0.0652	1.5446	1.5448	0.208	4.808	1.145	7.4
0.4992	0.0978	1.5120	1.5122	0.175	5.714	2.051	12.6
0.4942	0.1304	1.4794	1.4796	0.143	6.993	3.330	19.6
0.4892	0.1630	1.4468	1.4470	0.110	9.091	5.428	31.1
Run 27:		$c_o = 1.337 \times 10^{-5}$.					
0.5128	0	1.6100	1.6100	0.273	3.663		
0.5078	0.0326	1.5774	1.5774	0.240	4.167	0.504	2.5
0.5028	0.0652	1.5448	1.5448	0.208	4.808	1.145	7.0
0.4978	0.0978	1.5122	1.5122	0.175	5.714	2.051	12.6
0.4928	0.1304	1.4796	1.4796	0.143	6.993	3.330	19.6
0.4878	0.1630	1.4470	1.4470	0.110	9.091	5.428	31.0
Run 29:		$c_o = 1.365 \times 10^{-5}$.					
8.4586	0	1.6100	1.6100	0.245	4.082		
8.4536	0.0326	1.5774	1.5774	0.212	4.717	0.635	2.9
8.4486	0.0652	1.5448	1.5448	0.180	5.556	1.474	10.2
8.4436	0.0978	1.5122	1.5122	0.147	6.803	2.721	23.0
Run 28:		$c_o = 1.377 \times 10^{-5}$.					
16.192	0	1.6100	1.6100	0.233	4.292		
16.187	0.0326	1.5774	1.5774	0.200	5.000	0.708	14.6
16.182	0.0652	1.5448	1.5448	0.168	5.952	1.660	32.0
16.177	0.0978	1.5122	1.5122	0.135	7.407	3.115	53.1

FIGURE 27

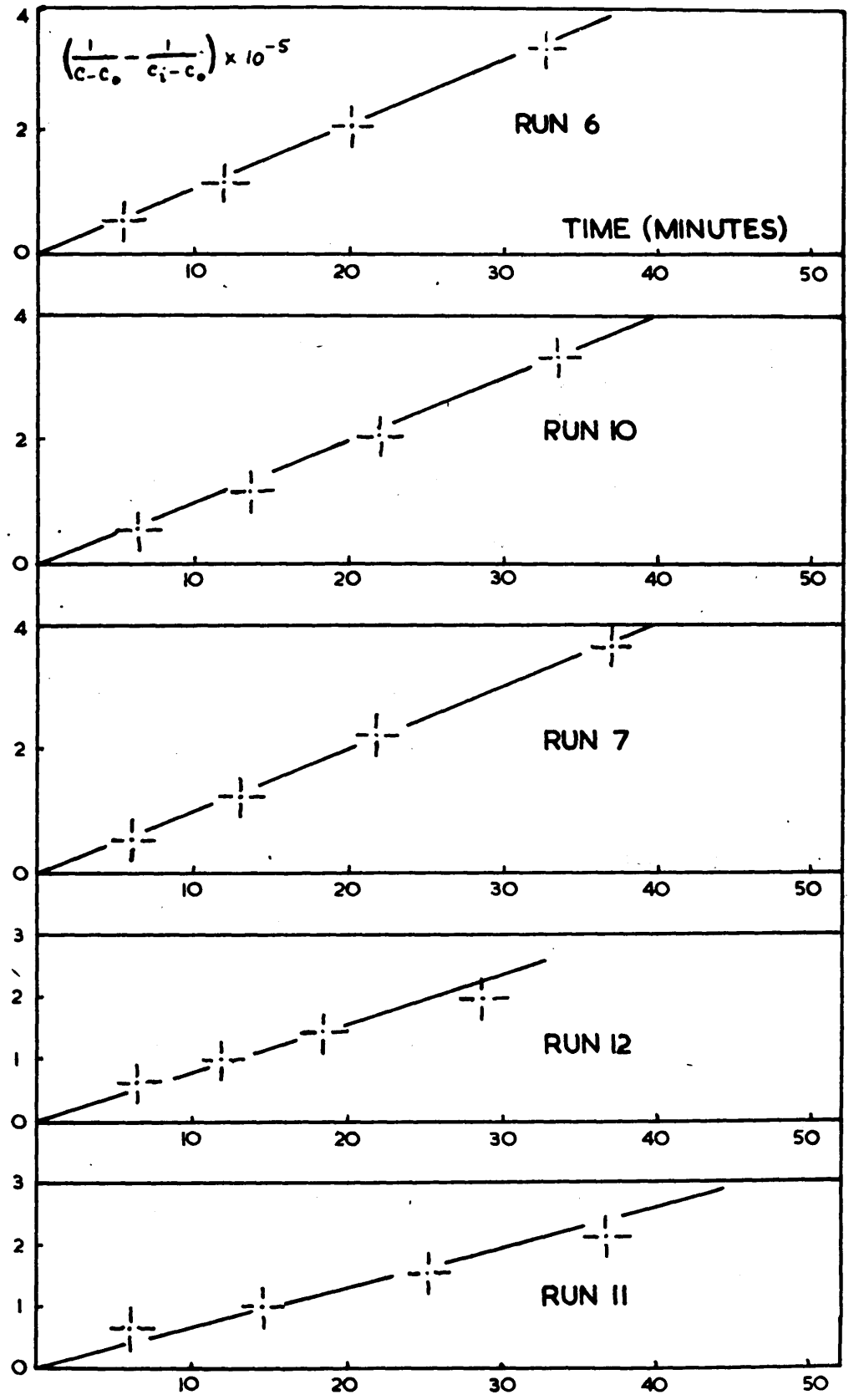
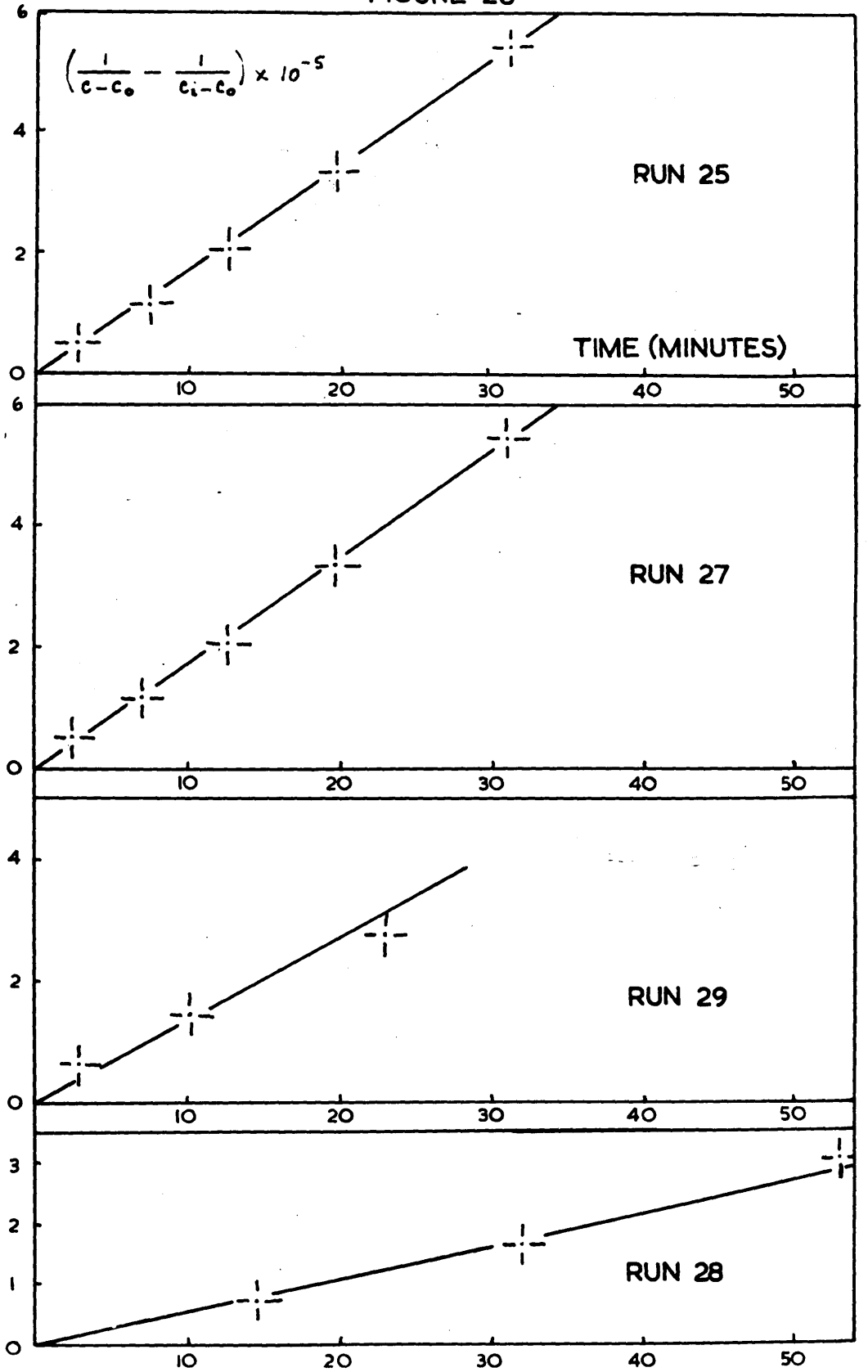

$\left(\frac{1}{C-C_o}-\frac{1}{C_i-C_o}\right)\times 10^{-5}$
RUN 6
TIME (MINUTES)
RUN 10
RUN 7
RUN 12
RUN 11
0
1
2
3
4
10
20
30
40
50

FIGURE 28


$\left(\frac{1}{c-c_o} - \frac{1}{c_i-c_o}\right) \times 10^{-5}$
RUN 25
TIME (MINUTES)
RUN 27
RUN 29
RUN 28
0
1
2
3
4
6
10
20
30
40
50

These are summarised in Table 22 and the reciprocal of the resistance is plotted against time for all the experiments in figure 29. The time plot of 1/R for run 25 is also included in figure 29 as a standard for experiments 34 and 35 in which suspension H was used. The curves obtained are smooth but in the presence of high adsorbate concentrations the amount of silver chloride precipitated was considerably reduced and changes in 1/R were correspondingly more difficult to measure. These experiments were, therefore, also interpreted in terms of the integrated form of the second order rate equation.

Detailed results of the experiments summarised in Table 22 are given in Table 23. The amount of crystallisation in run 21 is too small for accurate measurement.

When $\{1/(c - c_o) - 1/(c_i - c_o)\}$ was plotted against time for these experiments, straight lines passing through the origin were obtained. These are shown in figure 30 and the slopes are given in Table 24.

The presence of the surface active agents sodium octadecyl sulphate and sodium benzene sulphonate therefore does not alter the kinetics of crystal growth of silver chloride seed crystals from supersaturated solution, though a marked effect on the rate of growth is observed.

TABLE 22

Run	$[Ag^+]$ $\times 10^5$ g.equivs/l	$[Cl^-]$ $\times 10^5$ g.equivs/l	$[Ag^+][Cl^-]$ $\times 10^{10}$	[Adsorbate] $\times 10^5$ g.equivs/l	Sol. Prod. $\times 10^{10}$	* % Super-saturn.
Cell F : 3mls. suspension G : Adsorbate = sod. octadecyl sulphate						
18	1.6100	1.6100	2.592	-	1.788	45
19	1.6100	1.6100	2.592	0.0367	1.789	45
20	1.6100	1.6100	2.592	0.9209	1.791	45
21	1.6100	1.6099	2.592	4.883	1.802	44
Cell F : 3mls. suspension H : Adsorbate = sod. benzene sulphonate						
34	1.6099	1.6100	2.592	5.285	1.802	44
35	1.6100	1.6100	2.592	10.561	1.813	43

* Percentage Supersaturation =

$$\frac{\text{Initial concentration product - solubility product}}{\text{solubility product}} \times 100$$

FIGURE 29

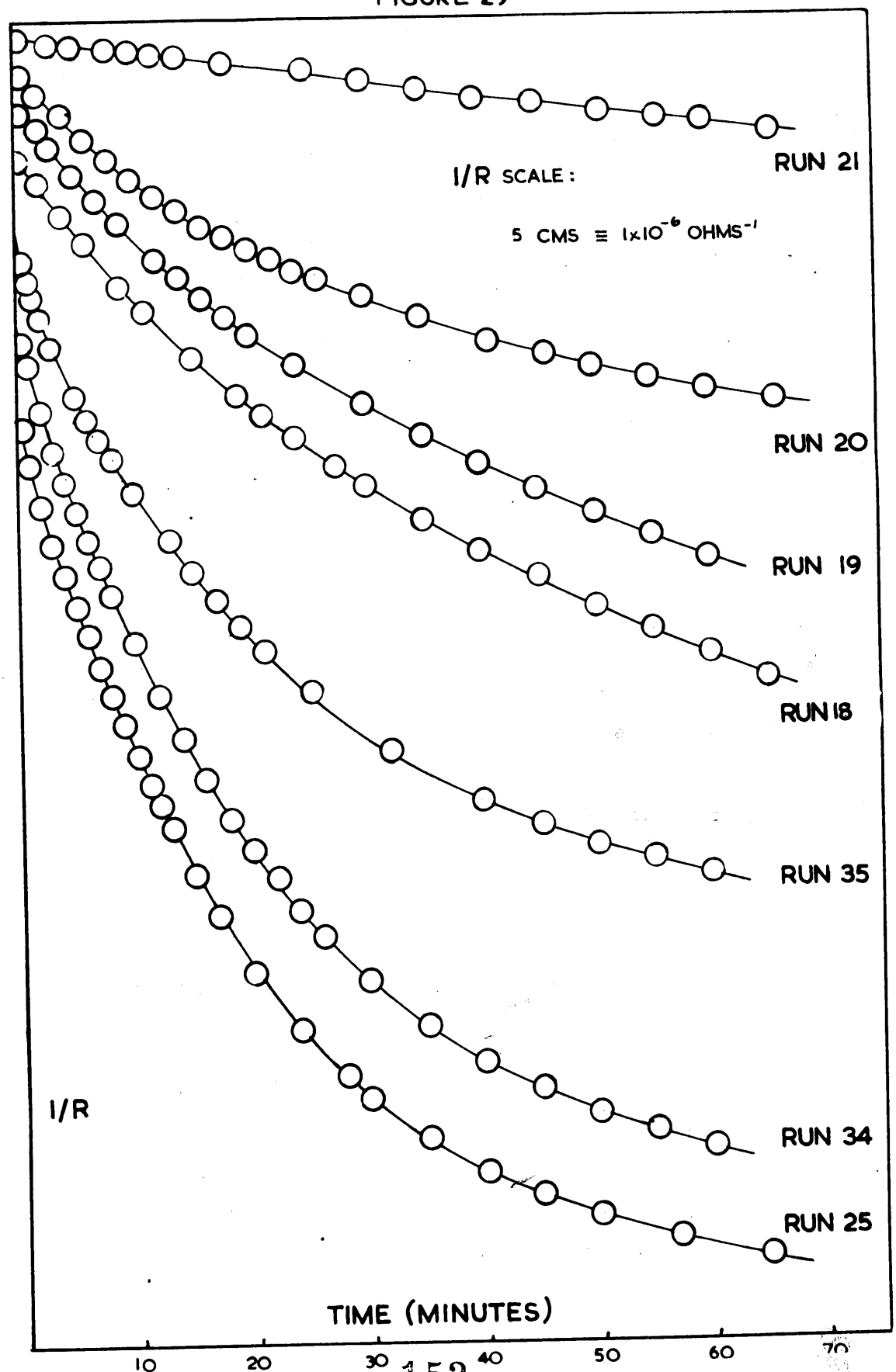

1/R SCALE:
5 CMS ≡ 1x10⁻⁶ OHMS⁻¹
RUN 21
RUN 20
RUN 19
RUN 18
RUN 35
RUN 34
RUN 25
1/R
TIME (MINUTES)
10
20
30
40
50
60
70

TABLE 23

$\frac{1}{R}-.10^5$	Amount AgCl preciptd. $\times 10^5$	$[Ag^+]$ $\times 10^5$ g.equiv/l	$[Cl^-]$ $\times 10^5$ g.equiv/l	$c-c_o$ $\times 10^5$	$\frac{1}{c-c_o}$ $\times 10^{-5}$	$1/(c-c_o) - 1/(c_i-c_o)$ $\times 10^{-5}$	Time (min)
Run 18:		$c_o = 1.337 \times 10^{-5}$.					
5.114	0	1.6100	1.6100	0.273	3.663		
5.089	0.0163	1.5937	1.5937	0.257	3.891	0.228	4.6
5.064	0.0326	1.5774	1.5774	0.240	4.167	0.504	9.7
5.039	0.0489	1.5611	1.5611	0.224	4.464	0.801	15.8
5.014	0.0652	1.5448	1.5448	0.208	4.808	1.145	23.8
4.989	0.0815	1.5285	1.5285	0.192	5.208	1.545	33.1
4.964	0.0978	1.5122	1.5122	0.175	5.714	2.051	44.7
Run 19:		$c_o = 1.337 \times 10^{-5}$.					
5.162	0	1.6100	1.6100	0.273	3.663		
5.137	0.0163	1.5937	1.5937	0.257	3.891	0.228	4.8
5.112	0.0326	1.5774	1.5774	0.240	4.167	0.504	10.5
5.087	0.0489	1.5611	1.5611	0.224	4.464	0.801	17.6
5.062	0.0652	1.5448	1.5448	0.208	4.808	1.145	26.9
5.037	0.0815	1.5285	1.5285	0.192	5.208	1.545	38.7
5.012	0.0978	1.5122	1.5122	0.175	5.714	2.051	52.6
Run 20:		$c_o = 1.338 \times 10^{-5}$.					
5.684	0	1.6100	1.6100	0.272	3.677		
5.659	0.0163	1.5937	1.5937	0.256	3.906	0.229	5.6
5.634	0.0326	1.5774	1.5774	0.239	4.184	0.507	13.3
5.609	0.0489	1.5611	1.5611	0.223	4.484	0.807	25.7
5.574	0.0652	1.5448	1.5448	0.207	4.831	1.154	54.5
Run 34:		$c_o = 1.343 \times 10^{-5}$.					
10.066	0	1.6100	1.6100	0.267	3.745		
10.016	0.0326	1.5774	1.5774	0.234	4.274	0.529	3.5
9.966	0.0652	1.5448	1.5448	0.202	4.951	1.206	8.4
9.916	0.0978	1.5122	1.5122	0.169	5.917	2.172	14.6
9.866	0.1304	1.4796	1.4796	0.137	7.299	3.554	22.4
9.816	0.1630	1.4470	1.4470	0.104	9.615	5.870	36.2
Run 35:		$c_o = 1.347 \times 10^{-5}$.					
14.886	0	1.6100	1.6100	0.263	3.802		
14.836	0.0326	1.5774	1.5774	0.230	4.348	0.546	4.1
14.786	0.0652	1.5448	1.5448	0.198	5.051	1.249	11.6
14.736	0.0978	1.5122	1.5122	0.165	6.061	2.259	21.7
14.686	0.1304	1.4796	1.4796	0.133	7.519	3.717	40.8

FIGURE 30

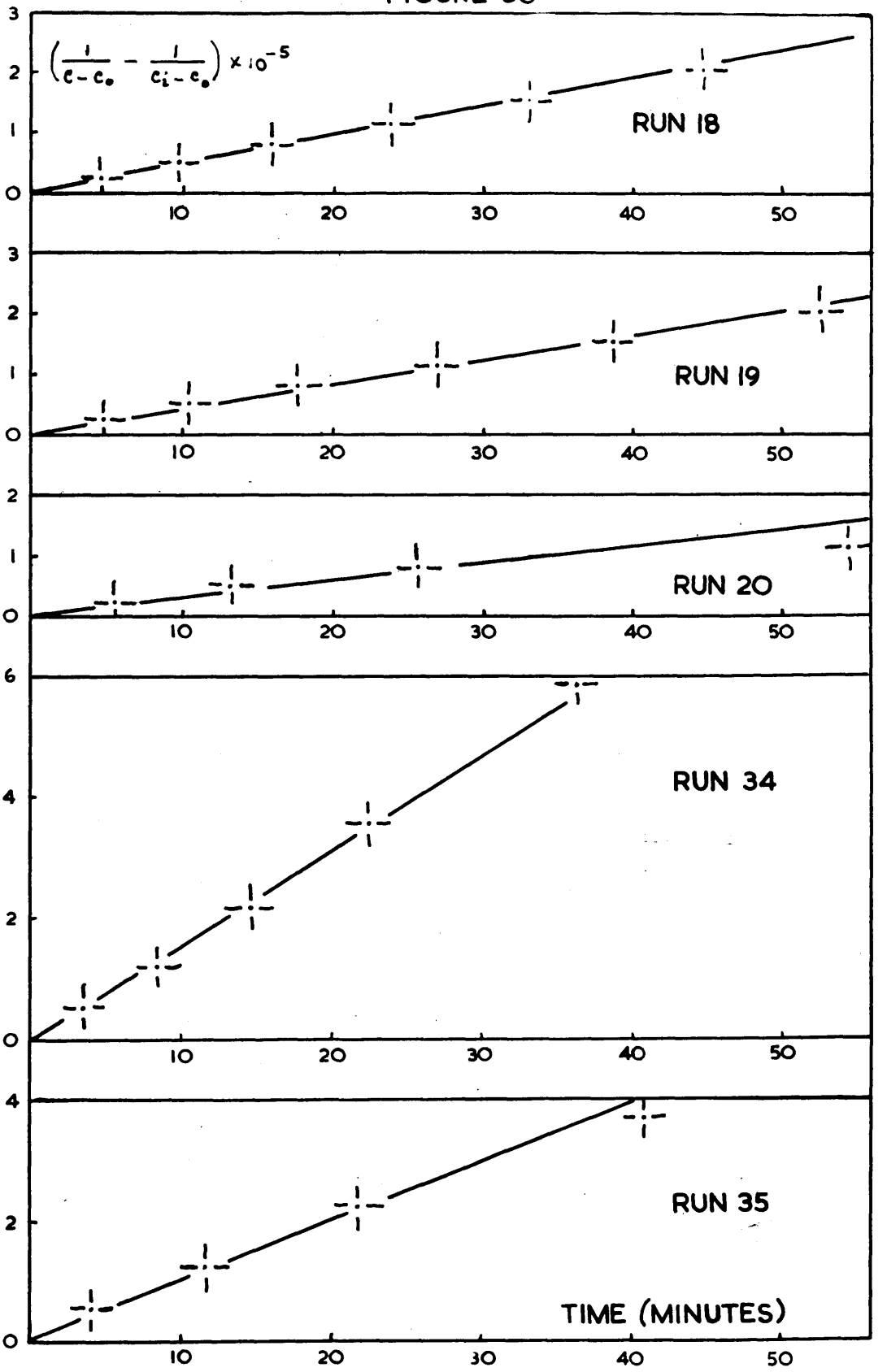

$\left(\frac{1}{c-c_o} - \frac{1}{c_i-c_o}\right) \times 10^{-5}$
RUN 18
RUN 19
RUN 20
RUN 34
RUN 35
TIME (MINUTES)
0
1
2
3
4
6
10
20
30
40
50

TABLE 24

Run	$I \times 10^5$ g.equivs/l.	$\sqrt{I} \times 10^3$	$K \times 10^{-4}$	Seed Suspension
6	3.206	5.66	1.04	F
10	3.206	5.66	0.98	F
7	13.23	11.5	1.00	F
12	53.12	23.0	0.80	F
11	77.40	27.8	0.65	F
25	3.206	5.66	1.70	H
27	3.206	5.66	1.70	H
29	53.57	23.14	1.35	H
28	103.30	32.14	0.55	H
18	3.206	5.66	0.49	G
19	3.243	5.70	0.42	G
20	4.127	6.42	0.30	G
21	8.090	8.99	-	G
34	8.491	9.22	1.50	H
35	13.767	11.73	1.00	H

DISCUSSION

In experiments 6 and 10 on the influence of ionic strength on the rate of growth of silver chloride seed crystals, no potassium nitrate was added to the supersaturated solutions and suspension F was used : the rate constants obtained were the same within experimental error. Experiments 25 and 27, done under similar conditions using suspension H, also gave reproducible rate constants. The average value of the rate constants, given in Table 24, is

1.02×10^4 for suspension F

and 1.70×10^4 for suspension H.

When the latter value was corrected as on page 123 for the difference in surface area of suspensions F and H, the value for comparison with 1.02×10^4 was 1.09×10^4. The ionic strength in experiments 12 and 29 is approximately the same and on comparing the rate constants K_{12} and K_{29} with 1.02×10^4 and 1.70×10^4 respectively, it is seen that the relative decrease in rate constant with increase in ionic strength is the same for experiments in which different seed suspensions are used.

i.e. Suspension F : $\frac{K_{12}}{1.02 \times 10^4} = \frac{0.80 \times 10^4}{1.02 \times 10^4} = 0.78$

Suspension G : $\frac{K_{29}}{1.70 \times 10^4} = \frac{1.35 \times 10^4}{1.70 \times 10^4} = 0.79.$

It has been shown that the value of the factor $1.02\ z_A z_B$ in the equation

$$\log k = \log k_o + 1.02\ z_A z_B \sqrt{I} \ ,$$

which gives the change in rate constant k with ionic strength I, should be approximately -1 for the reaction

$$Ag^+ + Cl^- \longrightarrow AgCl\ (s).$$

This means that changes in the rate of crystal growth of silver chloride with ionic strength are small and the best results would be obtained by measurement over a wide range of concentrations. In the conductimetric method used in the present work the range of ionic strengths which could be studied was limited. As the concentration of K^+ and NO_3^- ions in the supersaturated solutions is increased, the changes in conductivity due to precipitation become progressively smaller relative to the total conductivity of the solution and, therefore, more difficult to measure.

The value obtained for the factor 1.02 $z_A z_B$ in the present work was approximately -5. The fact that a negative value, though higher than expected, is obtained for the heterogeneous reaction studied is interesting, and investigation by other techniques at higher ionic strengths might provide more accurate data. Strict agreement with a theory which was developed for ionic reactions in homogeneous systems cannot be expected, but the change in k is in the right direction.

The experiments on the crystal growth of silver chloride seed crystals in the presence of surface active agents were an extension of the work of Davies and Nancollas[27] and, therefore, it is useful to establish that the rate constants obtained by these workers for experiments in supersaturated solutions with no added adsorbate can be compared with those obtained in similar experiments in the present work. The rate constants of Davies and Nancollas for their suspensions A and E were corrected for the surface area of suspension H used in the present work, and the value obtained, assuming comparable seed sizes in both investigations, was $1.7_6 \times 10^4$. This agrees with the experimental value $1.7_0 \times 10^4$ (Runs 25 and 27), indicating that the above assumption is justified.

In the course of the work using sodium octadecyl sulphate as adsorbate it was difficult to prepare solutions since though soluble at temperatures 60° and 100°C, the salt precipitated on cooling to give a cloudy solution. Only very dilute solutions of this salt could therefore be prepared. Similar but more serious difficulties were encountered in the preparation of solutions of sodium laurate and work with this salt was impossible. On the other hand, the sodium benzene sulphonate dissolved easily to give clear solutions at room temperatures.

From the experiments which have been carried out it appears that sodium octadecyl sulphate is a much more effective adsorbate than sodium benzene sulphonate but a more quantitative evaluation of the results is difficult in view of the difference in the solubility of the two salts. Although the amount of crystallisation in run 21 was negligible, further experiments at different concentrations of sodium octadecyl sulphate would be instructive to find out if the effect of this adsorbate can be compared with that of eosin. The growth rate of silver chloride in the presence of sodium benzene sulphonate does not appear to approach a limiting value in the concentration range studied.

The decrease in the rate of growth in all adsorbate experiments is relatively very much greater than the

decrease in the ionic strength experiments so that the effect of the surface active agents is not due to the increase in the ionic strength of the supersaturated solution. The results must be interpreted in terms of the decrease in the surface area available for growth due to adsorption of the foreign ions as suggested by Davies and Nancollas[27].

GENERAL DISCUSSION

From their experiments on the crystal growth of silver chloride seed crystals from aqueous supersaturated solutions, Davies and Jones[17] have postulated that a crystal in solution is surrounded by a monolayer of hydrated ions and that crystallisation takes place when a suitable aggregate of ions arrive simultaneously at a growth site, allowing the underlying ions to be dehydrated and enter the crystal lattice. The third order kinetics obtained in the present work for the crystal growth of silver chromate under similar conditions provides further evidence for this picture of crystallisation.

Davies and Nancollas have shown that the rate of dissolution of silver chloride seed crystals into water follows a complex kinetic equation[23]. They considered that the surface of a dissolving crystal was partly unhydrated and that the rate of solution was controlled by the rate at which exposed units of the crystal lattice entered the hydrated monolayer. They pointed out that more

detailed analysis of their solution kinetics was impracticable in view of the thickness of the diffusion layer surrounding the dissolving crystals, which could be a significant fraction of the distance between crystals in conditions where c/c_o , the ratio of the momentary concentration to its saturation value, was much less than unity.

In the present work the concentration gradient was reduced by measuring the dissolution of silver chloride and silver chromate into subsaturated solutions of these salts. In these conditions, first order kinetics were obtained, indicating that dissolution is controlled by the rate of transport of ions away from the crystal surface.

From all the above results it appears that crystallisation and dissolution are not reciprocal processes. Crystallisation is probably controlled by an adsorption reaction at the crystal face whereas in dissolution the physical process of diffusion determines the rate of reaction under specified conditions.

In any system crystallisation and solution will proceed concurrently and Davies and Jones[17] attempted to analyse the crystallisation of silver chloride in terms of two independent opposing processes in the following way :- If the concentrations, c, of silver and chloride ions in a solution are equal,

Rate of crystallisation of silver chloride $= k_1 s c^2$

Rate of solution of silver chloride $= k_2 s$,

where s is the surface area of solute and k_1 and k_2 are constants. In a saturated solution these rates are equal and so

$$k_2 = k_1 c_o^2 ,$$

where c_o is the solubility of silver chloride. In a supersaturated solution, assuming diffusion exerts no influence, the net rate of deposition will be given by

$$- dc/dt = k s (c^2 - c_o^2) \quad \ldots\ldots\ (1)$$

This was different from the equation

$$- dc/dt = k s (c - c_o)^2 ,$$

obtained experimentally, and Davies and Jones suggested that analysis into two independent opposing processes does not give a correct picture of a heterogeneous system where the amount of change at a particular reaction site is considered and not the total result of a number of isolated chemical reactions which have gone to completion. Experiments on the dissolution of silver chloride into subsaturated solutions could not be interpreted by the equation

$$dc/dt = k' s (c_o^2 - c^2), \quad \ldots\ldots\ (2)$$

the deviation being most marked in experiments at non-equivalent concentrations of silver and chloride.

The crystallisation and dissolution kinetics can be compared in a simple way by assuming that crystallisation is limited by the simultaneous arrival at a suitable growth site of the required aggregate of ions, whereas dissolution is limited only by the rate at which these ions can diffuse away from the crystal surface.

The work of Davies and Nancollas on the crystal growth of silver chloride from supersaturated solutions containing surface active agents[27] and their discovery that crystallisation could be delayed by using seed suspensions which had been aged in adsorbate solutions[28], provides further evidence of the importance of adsorption in the crystallisation process. This has been supported by the adsorbate experiments and the experiments on the influence of ionic strength in the present work.

APPENDIX

INTRODUCTION

The equilibria existing in aqueous solutions of chromates have been studied by several workers. The early investigation by Sherrill[41], who measured the freezing point of dilute solutions of chromic acid and potassium dichromate, indicated the importance of the intermediate hydrogen chromate ion in the dissociation of chromic acid and chromates. The main equilibria involved were those of the reactions

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^= \quad \ldots\ldots (1)$$

$$2HCrO_4^- \rightleftharpoons H_2O + Cr_2O_7^= \quad \ldots\ldots (2).$$

The relative amounts of $CrO_4^=$, $HCrO_4^-$ and $Cr_2O_7^=$ ions was dependent on the concentration of the solution and the values of the equilibrium constants of the reactions (1) and (2): qualitative values of these constants were derived.

More recently, Neuss and Riemann[40] measured the activity of hydrogen ions in solutions containing chromic acid and potassium chromate in fixed proportion, by means of a glass electrode. They obtained more quantitative values of

$$k_a = \frac{\{H^+\}\{CrO_4^{=}\}}{\{HCrO_4^-\}} = 3.20 \times 10^{-7}; \quad k_b = \frac{\{HCrO_4^-\}^2}{\{Cr_2O_7^{=}\}} = 2.3 \times 10^{-2}$$

at 25°C. Spectrophotometric measurements of k_b recently made by Tong and King[87] and Davies and Prue[42] have also given reliable values of k_b but no further verification of k_a was available.

In the present work the thermodynamic dissociation constant of the hydrogen chromate ion in aqueous solution has been derived from potentiometric measurements at 25°C. Solutions of 0.001 M chromic acid were titrated with standard sodium hydroxide solution in an atmosphere of nitrogen.

EXPERIMENTAL

Preparation of solutions.

The reservoir (capacity 500 mls.) of an automatic zeroing burette fitted with calcium chloride tubes, was filled with conductivity water and a rapid stream of nitrogen was bubbled through for about one hour to expel carbon dioxide. "Analar" sticks of sodium hydroxide were washed thoroughly with distilled water to remove carbonate and quickly added to the carbon dioxide - free water. The approximately 0.1 N solution of sodium hydroxide was standardised with 0.1 N hydrochloric acid.

A stock chromic acid solution was prepared as described previously (page 19) and fresh dilute solutions, approximately 0.001 M, were prepared for each titration.

Experimental Procedure.

150 mls. of a dilute chromic acid solution were pipetted into a clean dry 250 mls. beaker. A fairly rapid stream of nitrogen was passed through the solution so that it was efficiently stirred and kept free from carbon dioxide

during the subsequent titration. The beaker was supported in the water thermostat described on page 23 which was maintained at 25°C ± 0.01°C. The glass and calomel electrodes were immersed in the chromic acid solution and connected to the pH meter.

The solutions were left to come to temperature equilibrium before the pH of the chromic acid solution was measured. The standard sodium hydroxide solution was then added from the burette, first in 0.5 ml. portions and then in smaller volumes as each end-point was approached. The pH of the solution in the beaker was noted after each addition.

RESULTS AND DISCUSSION

A typical graph showing the change in pH during titration is given in figure 31. The concentrations of hydrogen chromate, chromate and dichromate ions in mixtures of chromic acid and sodium hydroxide were calculated from the pH values as follows :

$$pH = - \log \{H^+\} \quad \ldots\ldots (1)$$

The expression for the total chromium concentration in the solution, T_{Cr}, is

$$T_{Cr} = [CrO_4^{=}] + [HCrO_4^{-}] + 2\,[Cr_2O_7^{=}] \quad \ldots\ldots (2)$$

From electroneutrality considerations

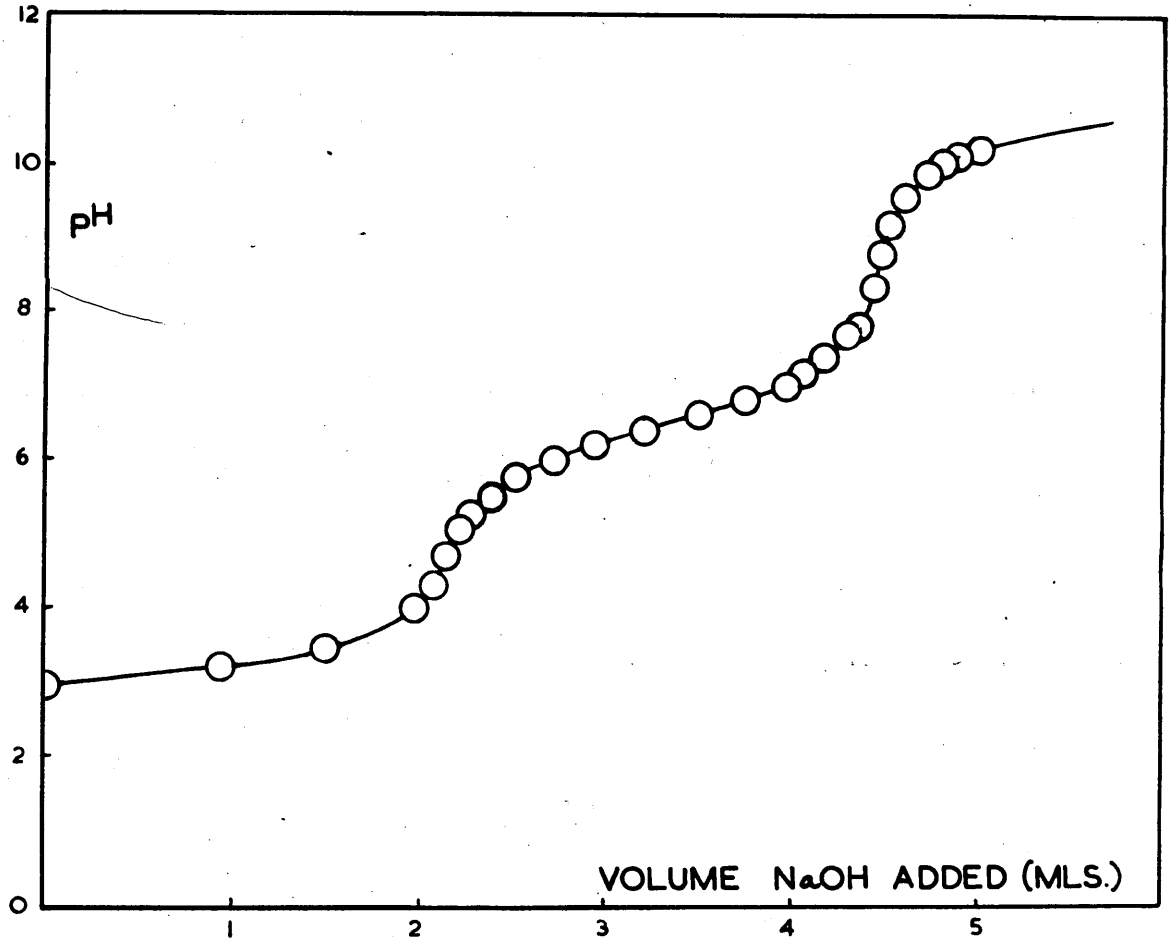
$$[Na^+] + [H^+] = 2\,[CrO_4^{=}] + [HCrO_4^{-}] + 2\,[Cr_2O_7^{=}] + [OH^-] \ldots (3)$$

From equations (2) and (3), neglecting the small concentration of hydroxide ions,

$$[CrO_4^{=}] = [Na^+] + [H^+] - T_{Cr} \quad \ldots\ldots (4)$$

The expression for the ionic strength, I, of the solution is

FIGURE 31



$$I = 0.5\left\{4[CrO_4^{=}] + [HCrO_4^{-}] + 4[Cr_2O_7^{=}] + [Na^+] + [H^+] + [OH^-]\right\}$$

or, using equation (2),

$$I = 0.5\left\{T_{Cr} + 3[CrO_4^{=}] + 2[Cr_2O_7^{=}] + [Na^+] + [H^+] + [OH^-]\right\}.$$

As a first approximation it was assumed that $[Cr_2O_7^{=}]$, $[H^+]$ and $[OH^-]$ were negligible and I was evaluated. The activity coefficients were then obtained from the Davies equation[50]

$$-\log f_z = 0.5\, z^2\left[\sqrt{I}/(1+\sqrt{I}) - 0.2\, I\right] \quad \ldots (6)$$

and $[H^+]$ was calculated from the pH of the solution. The $[CrO_4^{=}]$ could then be evaluated from equation (4). The dissociation constant, k_b, derived by Davies and Prue[42] was

$$k_b = [HCrO_4^{-}]^2 . f_1^2 / [Cr_2O_7^{=}] . f_2 = 3.03 \times 10^{-2} \quad \ldots (7)$$

Substituting equations (2) and (4) in equation (7),

$$k_b = \frac{[HCrO_4^{-}]^2}{\tfrac{1}{2}(2T_{Cr} - [Na^+] - [H^+] - [HCrO_4^{-}])} \cdot \frac{f_1}{f_2}$$

or $$\frac{2f_1^2}{k_b f_2}[HCrO_4^{-}]^2 + [HCrO_4^{-}] + ([Na^+] + [H^+] - 2T_{Cr}) = 0 \quad \ldots\ldots (8)$$

The $[HCrO_4^{-}]$ was evaluated from equation (8) and the $[Cr_2O_7^{=}]$ was then obtained from equation (2).

The final values of $[CrO_4^{=}]$, $[HCrO_4^{-}]$ and $[Cr_2O_7^{=}]$ were calculated by successive approximation of the ionic strength.

The thermodynamic dissociation constants

$$k_a = \frac{\{H^+\}[CrO_4^{=}]}{[HCrO_4^{-}]} \cdot \frac{f_2}{f_1}$$

derived from several titrations at various points in the pH range 6 to 7 are given, together with the concentrations of ionic species, in Table 25. The results of Neuss and Riemann at the lowest ionic strength studied by these workers have been recalculated by the above method and are given in the last five lines of Table 25. The mean k_a value is 3.06×10^{-7} mole/l. which may be compared with 3.20×10^{-7} mole/l., the original value of Neuss and Riemann. The mean value of k_a derived from the results of the present work was 3.01×10^{-7} moles/l. which is in good agreement with the value 2.9×10^{-7} moles/l. obtained from spectrophotometric measurements in these laboratories[88].

TABLE 25

T_{Cr} x10^3 moles/l.	[NaOH] x10^3 moles/l.	pH	[$CrO_4^{=}$] x10^3 moles/l.	[$HCrO_4^{-}$] x10^3 moles/l.	I x 10^3 moles /l.	k_a x 10^7
1.178	1.477	6.02	0.300	0.827	1.83	3.01
1.177	1.572	6.19	0.396	0.746	2.00	2.95
1.176	1.596	6.22	0.420	0.719	2.05	3.03
1.175	1.690	6.36	0.515	0.628	2.24	3.06
1.174	1.713	6.40	0.539	0.610	2.28	2.99
1.173	1.820	6.55	0.647	0.507	2.49	3.04
1.172	1.857	6.61	0.685	0.466	2.56	3.05
1.164	1.846	6.63	0.683	0.465	2.55	2.91
1.171	1.932	6.72	0.761	0.396	2.71	3.07
1.171	1.956	6.77	0.785	0.371	2.76	3.02
					mean $k_a = 3.01 \times 10^{-7}$.	
1.134	-	6.39	0.568	0.542	10.4	3.06
2.136	-	6.41	1.068	0.991	10.4	3.10
3.480	-	6.42	1.740	1.545	10.4	3.11
4.956	-	6.45	2.478	2.117	10.4	3.05
5.090	-	6.46	2.545	2.166	10.4	2.96
					mean $k_a = 3.06 \times 10^{-7}$.	

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